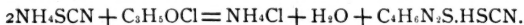


AMERICAN CHEMICAL JOURNAL.

ON PROPIMINE SULPHOCYANIDE.

By J. TSCHERNIAC AND T. H. NORTON.

If monochlor-acetone be exposed to the action of ammonium sulphocyanide in alcoholic solution, the sulphocyanide of a new base is formed according to the following reaction :

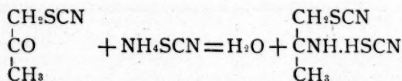


This reaction takes place even when the monochlor-acetone is in large excess.

Later experiments showed us that this new compound is the result of two successive reactions. In the first of these,



acetone sulphocyanide is formed. In the second reaction this latter compound is decomposed by ammonium sulphocyanide, the formation of the sulphocyanide $\text{C}_3\text{H}_6\text{N}_2\text{S.HSCN}$ being accompanied by the separation of a molecule of water :



We have given the name of propimine sulphocyanide to the base $\text{C}_3\text{H}_6\text{N}_2\text{S}$, as expressing most exactly its composition.

Preparation of the Sulphocyanide of the new base.—Two parts of ammonium sulphocyanide are dissolved in six parts of warm 90 per cent. alcohol; one part of monochlor-acetone is then added to the solution, which is allowed to stand for 24 hours. The precipitated ammonium chloride is then removed by filtration and washed with absolute alcohol. The filtrate and the alcohol used in washing are next evaporated on the water-bath, and the residue is dissolved in four times its weight of cold water. After standing for several days, a thick, viscous precipitate separates from the deep red solution, which is carefully decanted. The solution thus obtained is decolorised by boiling several times with animal charcoal, and is then concentrated to 110° . On cooling, the sulphocyanide of the new base is deposited in the form of thick crystalline crusts, while the ammonium salts which are present remain in the residual liquors. The sulphocyanide is obtained in a state of purity by renewed treatment with animal charcoal and recrystallisation. This method of preparation furnishes one-third of the theoretical yield.

The analysis resulted as follows :

- (1) 0.3955 gram gave 0.149 gram H_2O , and 0.510 gram CO_2 .
- (2) 0.2365 gram gave 0.0571 gram N by Will and Varrentrap's method.
- (3) 0.2305 gram gave 0.0552 gram N by Dumas' method.
- (4) 0.202 gram gave 0.5393 gram $BaSO_4$ by Carius' method.
- (5) The sulphocyanic acid was titrated by Volhard's method, and the precipitated silver sulphocyanide was weighed.

	Calculated.	(1)	(2)	(3)	Found.	(4)	(5)
C _s	34.68	35.17	...	...	...	...	...
H ₇	4.04	4.12	...	...	...	...	...
N ₃	25.28	...	24.14	23.95	...	...	...
S ₂	37.0	...	...	...	36.63	...	...
HSCN	34.1	...	...	...	...	34.0	34.2 34.45

This salt is obtained in the form of large, handsome crystals, usually of a light yellow color, but almost colorless when in a state of great purity. It melts at 114° – 115° , becomes red at 175° , and is decomposed above this temperature. It is very soluble in alcohol and hot water, from the latter of which it is easily crystallised. The aqueous solution gives all the ordinary reactions of soluble sulphocyanides. The free base is obtained in the form

of colorless drops when potash is added to the strongly concentrated solution.

Nitrate of Propimine sulphocyanide, $C_4H_6N_2S.HNO_3$, results from the double decomposition of the salt just described with silver nitrate, or from the neutralisation of the free base with nitric acid. It crystallises in the form of colorless needles from its aqueous solution, melts at 183° , and is decomposed with detonation above 200° .

0.325 gram gave 0.1265 gram H_2O and 0.321 gram CO_2 .

Calculated for $C_4H_6N_2S.HNO_3$.

C	27.12
H	3.95

Found.

26.94
4.30

Sulphate of Propimine sulphocyanide, $C_4H_6N_2S.H_2SO_4.2H_2O$, is obtained in a similar manner. It crystallises from the aqueous solution in the form of small white needles.

Calculated.

H_2SO_4	39.51
-----------	-------

Found.

40.09

Chloroplatinate of Propimine sulphocyanide, $(C_4H_6N_2S.HCl)_2PtCl_2$, is obtained in the form of a brownish yellow powder when platinum chloride is added to the solution of the base in hydrochloric acid.

0.301 gram gave 0.092 gram Pt.

Calculated.

Pt	30.80
----	-------

Found.

30.66

Preparation of the free base.—A concentrated solution of caustic potash is added in slight excess to pure crystals of the sulphocyanide described above. The liberated base is extracted by means of ether; the ethereal solution is dried over potash; and after driving off the ether on the water-bath, the base is obtained in a state of purity by distillation in a vacuum on an oil-bath.

The base is thus obtained in the form of a colorless, crystalline mass melting at 42° . This compound exhibits in a striking manner the phenomenon of surfusion. When once melted, congelation does not ensue until the temperature has fallen to 28° . As soon as the congelation has commenced, the temperature mounts to 42° , and remains unchanged up to the end of the solidification. It distills at 136° without decomposition under a pressure of 3-4 cm. of mercury. Under ordinary atmospheric pressure it distills at 231° – 232° , but undergoes a slight decomposition. It is exceedingly

hygroscopic, and very soluble in water, alcohol and ether. The aqueous solution possesses an alkaline reaction. When preserved in bottles which are not hermetically closed, it slowly blackens, and finally gives rise to products of a resinous nature.

0.374 gram gave 0.753 gram BaSO_4 .

	Calculated.	Found.
S	28.07	27.64

CH_3SCN
Acetyl-propimine sulphocyanide, $\begin{array}{c} \text{CN} \cdot \text{C}_2\text{H}_3\text{O} \\ | \\ \text{CH}_3 \end{array}$. This compound

is obtained by mixing equal weights of the free base and of acetic anhydride. The reaction is accompanied by a notable evolution of heat, and is completed by warming on the water-bath. After adding water and neutralising with potassium carbonate, the acetyl compound separates in the form of hard white crusts. These are rubbed together with a small amount of water in a mortar, and the water is drawn off by means of a vacuum pump. The compound is obtained in a state of purity by dissolving in ten times its weight of boiling water, allowing to crystallise, and drying the crystals over sulphuric acid. The yield is nearly theoretical. The white, fine silky crystals prepared in this manner possess a brilliant diamond lustre. They melt at 134° , and solidify at 91° . They are but slightly soluble in cold water; the solubility is, however, notably increased by the addition of acids or caustic alkalies.

0.274 gram gave 0.462 gram CO_2 and 0.135 gram H_2O .

	Calculated.	Found.
C	46.15	45.98
H	5.13	5.47

CH_3SCN
Hydroiodide of Methyl-propimine sulphocyanide, $\begin{array}{c} \text{CNCH}_3 \cdot \text{HI} \\ | \\ \text{CH}_3 \end{array}$

Equal molecular weights of methyl iodide and propimine sulphocyanide are brought together. The reaction, which is extremely violent at first, is completed by heating for several hours on a water-bath. The yield is theoretical. By crystallisation in water the product is easily purified. It is thus obtained in the form of brown,

transparent scales. It melts at 159.5° ; is soluble in two parts of hot water and ten parts of cold water.

0.383 gram gave 0.323 gram CO_2 and 0.1475 gram H_2O .

0.242 gram gave 0.215 gram AgI .

	Calculated.	Found.
C	23.44	22.97
H	3.52	4.25
I	49.60	49.42

The free methyl-propimine sulphocyanide cannot be distilled without decomposition.

Laboratory Notes from the University of Cincinnati.

XXVII.—ON SOME PHOSPHIDES OF IRIDIUM AND PLATINUM.

BY F. W. CLARKE AND O. T. JOSLIN.

In May, 1881, Mr. John Holland, a manufacturer of gold pens in Cincinnati, took out a patent for a process of fusing iridosmine. For pointing gold pens, only selected grains of the native mineral were suitable; and his object was to utilise the quantities of unavailable mineral which accumulated in his establishment. His process, briefly stated, consisted in heating the ore to whiteness, and then throwing in upon it common phosphorus; fusion at once took place, and the excess of phosphorus was afterwards removed by heating the product in contact with lime. The metal thus produced was harder than steel, brilliantly lustrous, insoluble in acids, and available for a great variety of purposes. As the process has already been fully described by Professor W. L. Dudley,¹ it needs no further technical discussion here. Our work relates to the chemical side of the new iridium industry.

At an early date, samples of the "fused iridium" were placed in our hands for examination, together with some of the original ore from which the melts had been made. The latter was a Californian iridosmine, in hard, brilliant grains, of specific gravity 19.182. Of the fused product the sp. gr. was only 13.768.

¹ Sci. Proc. Ohio Mechanics Institute, Jan, 1882.

Two portions of the latter were prepared at different times, for comparison with the native mineral, and partial analyses were made. In the first portion, phosphorus only was determined, three estimations giving respectively 7.52, 7.58, and 7.74 per cent. This portion contained barely a trace of osmium.

In the iridosmine itself 15.38 per cent. of osmium were found; and accordingly the second fused portion was examined with special reference to this element. As far as it was carried out, the analysis gave the following results:

Iridium,	80.82
Osmium,	6.95
Phosphorus,	7.09
Ruthenium and Rhodium,	7.20
	102.06

No attempt was made to separate the ruthenium and rhodium, nor to trace out the cause of the plus error. The phosphorus agrees reasonably well with the estimations made in the first portion; and the low percentage for osmium, compared with the mere trace in the other lot and the large amount in the ore, shows that this element is more or less eliminated according to the circumstances attending fusion. The "fused iridium" is plainly, as might be expected, a phosphide; and the percentage of phosphorus indicates a compound having the formula Ir_2P . For this formula the percentage of phosphorus should be 7.43, and evidence in its favor will appear farther on. Of course the product is far from pure, containing the phosphides of the other metals of the group; but its general nature is evident. With pure iridium as the starting point, a pure Ir_2P would probably be obtained.

Since it seemed desirable to ascertain how platinum would behave when treated like the iridium, experiments in that direction were undertaken. The metal used was a worn-out platinum crucible, carefully cleaned, of which a sample was first analysed. The results were as follows:

Platinum,	97.22
Iridium,	2.49
Copper,	.46
Palladium,	a trace
	100.17

15.4200 grams of this material were heated to whiteness in a hessian crucible, and 20 grams of stick phosphorus were thrown in. Fusion at once took place, and when the excess of phosphorus had burned off, the mass was allowed to cool. We thus obtained a brilliant, silver white, brittle button, weighing 19.4663 grams. As it was porous, we did not determine its specific gravity. If we reckon the iridium in the mass as platinum, and ignore the trifling amount of copper, the increase in weight gives us synthetically the following composition for the product :

	Found.	Calculated for Pt_3P_8 .
Platinum,	79.21	79.05
Phosphorus,	20.79	20.95
	100.00	100.00

These figures are useful only in confirmation of our subsequent analyses.

A portion of the phosphide, coarsely powdered, was next boiled for at least forty hours with aqua regia. At the end of that time a considerable portion was still undissolved, and trial showed it to be quite insoluble in the reagent. The soluble portion amounted to 71.21 per cent. of the whole, and the insoluble part to 28.79 per cent. The latter, dissolved by fusion with sodium nitrate and caustic soda and subsequent boiling with aqua regia, was analysed separately, and proved to be a definite phosphide of the formula PtP .

	Found.	Calculated for PtP .
Platinum,	86.16	86.28
Phosphorus,	14.03	13.72
	100.19	100.00

The soluble fraction, also analysed independently, agreed approximately with the formula PtP_2 .

	Found.	Calculated for PtP_2 .
Platinum,	76.62	75.88
Phosphorus,	23.68	24.12
	100.30	100.00

Recalculating the analyses of the two fractions so as to express the composition of the original phosphide, we get the following results to compare with those obtained by synthesis.

	Found, analysis.	Found, synthesis.	Calculated for Pt_3P_5 .
Pt,	79.39	79.21	79.05
P,	20.87	20.79	20.95
	100.26	100.00	100.00

The data for the foregoing calculations, in weights, are as follows: Weight of sample, 2.2042 grams. Dissolved, 1.5695 gram; undissolved, .6347 gram. Platinum in the soluble portion, 1.2025 gram; in the insoluble, .5475 gram; total, 1.7500 gram. Phosphorus in the soluble portion (calculated from weight of $Mg_2P_2O_7$), .3717 gram; in the insoluble, .0891 gram; total, .4608 gram. These figures further show that the ratio between the dissolved and insoluble phosphides agrees well with the equation $Pt_3P_5 = PtP + 2PtP_2$.

	Found.	Calculated.
Insoluble PtP,	28.79	30.54
Soluble PtP_2 ,	71.21	69.46
	100.00	100.00

The slight discordance here, 1.75 per cent., taken together with the fact that the platinum in the soluble part came out rather too high, shows that a trifling quantity of the PtP was dissolved by the very prolonged action of the aqua regia to which it had been subjected. In other words, the fractionation of the Pt_3P_5 into the two simpler phosphides is not quite perfect.

In order to determine whether the complex phosphide Pt_3P_5 could be reduced to metal by long heating, two portions were roasted in a muffle until constant weight was obtained. The losses in weight were 14.08 and 13.78 per cent. respectively. The product of this roasting was malleable, and readily soluble in aqua regia. It contained 7.36 per cent. of phosphorus, which is just the amount required by the formula Pt_3P . Here then we have a fourth phosphide analogous in composition to the fused iridium, and confirmatory of the formula assigned to the latter. The reduction of Pt_3P_5 to Pt_3P should require a loss of 14.66 per cent. In all of these calculations we have taken 195 for the atomic weight of platinum. The trace of copper in the original platinum did not show itself in any of the analyses of the phosphides, and the small amount of iridium present could nowhere affect our results by more than a hundredth of a per cent.

In conclusion, our experiments show the existence of three simple phosphides of platinum, PtP_2 , PtP , and Pt_2P , and of a double phosphide Pt_3P_5 . Of these compounds the monophosphide, by virtue of its insolubility in aqua regia, is the most noteworthy. The compound PtP_2 is probably identical with the phosphide described by Schrötter,¹ who obtained it, as well as analogous phosphides of iridium and palladium, by heating the finely divided metal in phosphorus vapor. As far as we can learn, no other platinic phosphides have ever been regularly analysed. Pelletier² heated platinum with phosphorus and found that 300 grains of the former took up 54 of the latter; results which approximate roughly to the ratio PtP . Edmund Davy³ tried two sets of experiments in the same direction. First, he heated ammonium chloroplatinate with phosphorus, and obtained a black compound of doubtful composition. Afterwards he heated platinum and phosphorus together in a vacuum, and obtained results which, calculated synthetically, agree well with the formula Pt_3P_4 . This product was insoluble in strong acids, and at the time (1812) could not be directly analysed.

XXVIII.—ON CADMIUM IODIDE.

By F. W. CLARKE AND E. A. KEELER.

Of late years the suggestion has repeatedly been made, by various chemists, that the definite series of related chemical elements may be analogous in character to series of compounds such as the hydrocarbons. For example, fluorine, chlorine, bromine, and iodine form one such series; the nitrogen group, from nitrogen to bismuth, forms another, etc. There have been many efforts to trace relationships between the atomic weights in these and other similar series, and so to get evidence in favor of the foregoing hypothesis; but except in the establishment of the periodic law, all such attempts seem to have ended fruitlessly.

But notwithstanding the failure to discover definite numerical relations between the elements, the evolutionary speculation is suggestive. If the series of elements are developed progressively, like

¹ Sitzungsberichte Wien Akad. 1849, 301.

² Ann. de Chimie, 13, 1792, 101-143.

³ Tilloch's Mag. 40, 1812, 27-39. Schweigg. Journ. 10, 382.

series of compounds, there should be various points of comparison; and one line of thought is as follows. In any series of compounds, the possibility of isomerism increases as we ascend; and therefore, by analogy, we should expect to find a similar state of affairs among the so-called elements. The derivatives of the highest member of a series should be more numerous and complex than those of lower members, and cases of allotropy or isomerism ought also to be more frequent. Whether this is so or not in all known instances we do not attempt to say; our experiments bear upon a single point, and that may be stated briefly.

It is a well-known fact that allotropy is common among the metallic iodides, and much more so than among the corresponding compounds of chlorine and bromine. For example, the scarlet and yellow modifications of mercuric iodide, and the three varieties of antimony iodide may be cited. We have been engaged in the study of several other iodides, especially that of cadmium, and in this case we are now prepared to announce the existence of two distinct modifications. So far then our results lend countenance to the speculative idea which we began by quoting, even though much weightier evidence would be needed to put it upon the basis of a clear and definite theory. The speculation, however, instigated our experiments, and in their success its utility as a means of stimulating research is justified.

Up to the present time but two determinations of the specific gravity of cadmium iodide have been published. First, by Bödeker, who found it to be 4.576 at 10° ; and second, by Fullerton, whose mean result was 5.9798. The latter determination was made some years ago in this laboratory, and is undoubtedly too high; but the discordance between the two is so great that it could hardly be ascribed to error. Accordingly, we prepared cadmium iodide by a variety of methods, and obtained the following determinations of specific gravity. All weighings were made in benzene, and the results are referred to water at 4° as unity. Our mean figures may be stated first, and the details given later.

A. Cadmium and iodine, in equivalent quantities, were heated together in a sealed tube from which the air had been exhausted. The product was white, and contained 1.30 per cent. of residue insoluble in water. Its character was established by analysis, and we found it to contain about 98.5 per cent. true CdI_2 . Sp. g. 5.543.

B. Cadmium and iodine were digested together under water.

The crystals obtained by evaporation were carefully identified as CdI_2 . Sp. g. 5.622.

C. A very fine sample of iodide prepared by Schuchardt, of Goerlitz, was examined. Its mode of preparation, as stated in a letter from the maker, consisted in dissolving together equivalent quantities of cadmium sulphate and potassium iodide, evaporating to dryness, extracting with alcohol and crystallising. Sp. g. 5.660.

D. Preparations A and B were mixed and recrystallised from alcohol. The sp. g., as determined by Mr. E. Twitchell, was 5.701.

So far at least the variations in our results were not startling. Our next series came out differently.

E. Cadmium carbonate was dissolved in hydriodic acid. The solution, discolored by free iodine, was rendered nearly colorless by cadmium clippings, and crystallised. Sp. g. 4.612. A second series of determinations gave 4.596. Both figures agree well with Bödeker. The salt was analysed, with results as follows:

	Found.	Calculated for CdI_2 .
Cadmium,	30.40	30.60
Iodine,	69.33	69.40
	99.73	100.00

F. To verify these results, if possible, another lot of iodide was prepared with carbonate and acid, but the solution was not decolorised by metal. Sp. g. 5.729. The sample on analysis yielded 30.56 per cent. of cadmium.

G. Another solution was prepared as under F, and divided into two parts. One was allowed to evaporate spontaneously at a low temperature. Sp. g. of product 5.610.

H. The second part of solution G was boiled down rapidly. Sp. g. of iodide 5.675.

I. Metallic cadmium was dissolved in hydriodic acid. The solution yielded a pure iodide of sp. g. 4.688, as determined by Mr. Twitchell. This preparation dried at 50° , became silver grey and its sp. g. rose to 5.141. Again heated to 50° the sp. g. rose to 5.536. A third heating brought it up to 5.545. Accompanying this change there was a little decomposition which resulted in the formation of a trifling amount of insoluble material.

The foregoing results all point pretty definitely to the existence of two allotropic varieties of cadmium iodide, differing in specific gravity by about a unit. The higher density represents a union of cadmium and iodine with little or no change of volume, while the lower corresponds to a noteworthy expansion and consequent instability. The higher or normal salt, which we may call α cadmium iodide, is white, and undergoes no perceptible change when heated to any temperature below 250° . The lower or β salt is brownish, and loses weight even at 40° . One sample lost 5.50 per cent. at 50° , an alteration which is undoubtedly due to the formation of an oxide or oxyiodide with liberation of iodine. The increase in specific gravity upon heating may be partly due to the same change, but is mainly ascribable to a transformation of the β into the α modification. The conditions governing the formation of the new salt are obscure and need farther study. In our experiments we obtained it only twice, and in each case cadmium was acted upon by hydriodic acid. In the first instance, however, this action was only incidental to the decolorisation of a solution of iodide otherwise prepared, and was necessarily very trifling. In both cases, however, cadmium iodide was exposed to the action of nascent hydrogen, and it is probable that the latter had something to do with the production of the β compound. This suggestion we offer merely as a clue for use in further study, without any speculations as to just how the reactions proceeded.

In detail, our specific gravity determinations were as follows, including the temperatures of weighing. The series are lettered as before :

I. The normal CdI_2 .

A.	B.	C.	D.
5.539, 20.4°	5.622, 15.2°	5.697, 17.5°	5.716, 14.8°
5.530, 20.1	5.618, 15.2	5.704, 18.	5.714, 15.3
5.530, 20.1	5.638, 15.2	5.630, 18.2	5.696, 15.5
5.574, 20.2	5.629, 15.4	5.650, 18.1	5.696, 15.8
5.543, 19.9	5.630, 15.6	5.642, 18.2	5.685, 15.9
5.543, 19.9	5.621, 16.1	5.626, 18.2	
5.523, 19.8	5.610, 16.6	5.672, 18.2	
5.564, 20.1	5.611, 16.6		
5.543	5.622	5.660	5.701

F.	G.	H.
5.750, 10.5°	5.580, 17.6°	5.682, 15.0°
5.740, 10.5	5.610, 17.4	5.654, 15.2
5.715, 10.6	5.660, 17.7	5.683, 15.1
5.747, 10.5		5.682, 15.0
5.719, 10.6		
5.705, 10.6		
5.729	5.610	5.675
Total, 41 weighings.	Mean of all, 5.644.	

II. β CdI₂.

E ₁ .	E ₂ .	I.
4.618, 14.0°	4.598, 15.2°	4.697, 18.8°
4.607, 14.4	4.594, 15.3	4.713, 18.9
4.609, 14.7	4.601, 15.2	4.740, 19.0
4.618, 15.0	4.602, 15.2	4.668, 19.0
4.612, 15.1	4.592, 15.4	4.625, 18.9
4.615, 15.1	4.593, 15.4	
4.605, 15.2	4.595, 15.2	
4.612	4.596	4.688

Total, 19 weighings. Mean of all, 4.626.

Molecular volume, α salt, 64.8" " β " 79.2

Mol. vol. Cd + I₂, 64.3, when sp. g. iodine = 4.948 (Gay Lussac), and sp. g. Cd = 8.655 (Matthiessen).

In connection with these experiments a little work was done upon the double iodides of cadmium. Attempts were made to prepare such double salts with the iodides of lead and of thallium, but unsuccessfully. Mercuric iodide dissolved freely in a hot solution of cadmium iodide, and the liquid, upon cooling, deposited scarlet crystals of the first-named salt unaltered. The mother liquor from these crystals, upon longer standing, yielded golden laminae, which were recrystallisable from hot alcohol. They were anhydrous, and contained iodine, cadmium and mercury. A partial analysis pointed to the formula CdI₂.3HgI₂.

	Found.	Calculated.
Cadmium,	6.90	6.48
Iodine,	58.80	58.98
Mercury,	34.30 by difference.	34.54
	100.00	100.00

There was not enough of this salt to admit of further investigation.

With other iodides we have not yet gone very far. Zinc iodide, prepared by direct union of the elements and sublimation in a stream of carbon dioxide, has a sp. gr. of 4.666.¹ Bödeker found a sp. gr. of 4.696. For a somewhat impure bismuth iodide from Schuchardt we found the sp. gr. to be 5.548. Bödeker's value was 5.652.

With stannic iodide we are still engaged. Suffice it to say that we are satisfied of the existence of at least two modifications, one darker red and less soluble in benzene than the other. But the difficulty of obtaining pure and definite products is very great, and we may not have time to complete the investigation.

XXIX.—SOME SPECIFIC GRAVITY DETERMINATIONS

BY F. W. CLARKE.

The following specific gravity determinations were made under my supervision by the students named below. The salts were weighed in benzene, and the density of water at 4° was taken as unity. Each figure is the mean of several closely concordant results.

Uranyl sulphate, $(\text{UO}_2)\text{SO}_4 \cdot 3\text{H}_2\text{O}$, 3.280 at 16.5°. H. Schmidt.

Uranyl ammonium sulphate, $(\text{UO}_2)\text{Am}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, 3.0131 at 21.5°. H. Schmidt.

Uranyl potassium sulphate, $(\text{UO}_2)\text{K}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, 3.363 at 19.1°. H. Schmidt.

Double salt, $\text{K}_2\text{CrO}_4 \cdot 2\text{Hg}(\text{CN})_2$, 3.564 at 21.8°. H. Schmidt.

Ferric chloride, sublimed, Fe_2Cl_6 , 2.804 at 10.8°. J. P. Grabfield.

Ferrous " FeCl_2 , 2.988 at 17.9°. J. P. Grabfield.

Chromic " violet, Cr_2Cl_6 , 2.757 at 15°. J. P. Grabfield.

Chromous " CrCl_3 , 2.751 at 14°. J. P. Grabfield.

The last compound contained 14 per cent. of chromic oxide as an impurity, and the sp. gr. actually found was 3.067. This, corrected by means of Schröder's value for Cr_2O_3 , 5.01, gives the sp. gr. assigned above.

¹ Value actually found, 4.736. This was corrected for 3.13 per cent. of admixed metal, becoming 4.666. There were six concordant estimations.

- Strontium chloride, cryst., $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, 1.964, 16.7° . E. Muehlberg.
 Cadmium chloride, CdCl_2 , 3.655, 16.9° . P. A. Knight.
 " bromide, CdBr_2 , 4.794, 19.9° . "
 " fluoride, CdF_2 , 5.994, 22.0° . E. A. Kebler.
 Thallium iodide, precipitated, TlI , 7.072, 15.5° . E. Twitchell.
 " " after fusion, TlI , 7.0975, 14.7° . E. Twitchell.
 " bromide, precipitated, TlBr , 7.540, 21.7° . H. Keck.
 " " after fusion, " 7.557, 17.3° . "
 Lead bromide, precipitated, PbBr_2 , 6.572, 19.2° . "
 Silver tartrantimonite, $\text{SbAgC}_4\text{H}_4\text{O}_7$, 3.4805, 18.2° . C. S. Evans.

XXX.—RESEARCHES ON THE TARTRATES OF ANTIMONY.

BY F. W. CLARKE AND CHARLES SETH EVANS.

Although some of the double tartrates of antimony, such as the tartar emetics, have been quite elaborately studied, our knowledge of its simple tartrates has hitherto been singularly inexact and vague. According to Bergmann,¹ a solution of antimonious oxide in aqueous tartaric acid crystallises confusedly; while according to Dulk¹ it does not crystallise at all. Berzelius² and Peligot³ both obtained large crystals, but assigned different formulæ; Berzelius without analysis, Peligot after investigation. Peligot, however, must have calculated his formula upon the basis of $\text{Sb}=129$, the old Berzelian determination; and his analysis, recalculated with the modern value of $\text{Sb}=120$, leads to no intelligible symbol. The precipitate formed by alcohol in solutions of the crystalline tartrate was also examined by Berzelius and by Peligot; and here again, upon incomplete analyses, different formulæ were based. In short, neither Berzelius nor Peligot studied these compounds at all thoroughly; and the subject, up to the time when we began our own experiments, was in a most confused state. Inferences were more numerous than facts, and the latter needed scrupulous reverification. We believe that we have succeeded in shedding some light upon the nature of the substances in question; and that

¹ See Gmelin's Handbook, edition of the Cavendish Society, 10, 297.

² Lehrbuch, 5 Aufl. 3, 1124.

³ Annales de Chim. et de Phys. 3 série, 20, 289.

the results which we have obtained may form a fair basis upon which to conduct future investigations.

Antimony trioxide, as is well known, is readily soluble in aqueous tartaric acid; but the properties of the solution depend upon the relative proportions of its constituents. When the oxide is dissolved in the acid to complete saturation, the solution yields no crystals whatever; but upon evaporation dries up to a gummy, amorphous mass. With less oxide and an excess of acid, crystallisation becomes possible, and in every case of this kind, rosettes of needles are obtained. If the acid is in slight excess, crystallisation takes place with difficulty, and the smaller the proportion of the oxide the more easily the crystals form. In all cases, however, in which the crystallisation occurs, the mother liquors are exceedingly viscous and consequently difficult to remove; so that it is by no means easy to secure pure products for examination. Furthermore, the crystals vary in composition, as the following percentages of antimony will show:

1. 40 grams of Sb_2O_3 were boiled with 60 grams of tartaric acid. The solution was incomplete. The filtered liquid, evaporated to dryness, gave a product containing 27.53 per cent. of antimony.

2. 35 grams Sb_2O_3 to 60 of acid. Yielded indistinct crystals which could not be purified for analysis.

3. 30 grams Sb_2O_3 to 60 of acid. Crystals washed and twice recrystallised. Per cent. of Sb, 18.92.

4. 20 grams Sb_2O_3 to 60 of acid. Product recrystallised. Several distinct lots of material gave crystals containing antimony in the following percentages:

A	13.35		
B	15.90		
C	16.48	16.64	
D	16.18	16.21	17.16
E	17.88	18.00	

The last product was dried with extreme care and examined further. The results will be given later.

5. 15 grams Sb_2O_3 to 60 of acid. Product recrystallised. Per cent. of Sb, 5.37. Probably a mixture.

6. 12 grams Sb_2O_3 to 60 of acid. Per cent. of antimony in crystals, 3.69 to 3.82. Probably a mixture.

The antimony was weighed as sulphide in every case, and the results indicate two things: First, the difficulty of obtaining definite products; and second, the probable existence of a series of salts. Two of the latter were analysed, as follows:

First. The crystals marked 3 and the preparation 4 E. of the foregoing table had all the characteristics of definite compounds. They proved to be identical, and to be closely represented by the formula $\text{Sb}(\text{C}_4\text{H}_4\text{O}_6)_3\text{H}_3.4\text{H}_2\text{O}$.

	3.	Found.	4 E.	Calculated.
Sb	18.92	17.88	18.00	18.78
C	22.59	22.98	23.19	22.53
H	3.78	3.39	3.78	3.60
Water at 120°	11.05		10.98	11.27

In brief, this tartrate, which may fairly be called antimonio-tritartaric acid, is simply a triple molecule of tartaric acid with half its replaceable hydrogen replaced by an atom of trivalent antimony. It crystallises in rosettes of white needles and is easily soluble in water. With carbonates it effervesces strongly and behaves like a weak acid. Its reactions in this particular will be considered further on. With alcohol its solution yields a copious white precipitate, which, washed with alcohol and thoroughly dried over sulphuric acid, proved to be neutral antimonious tartrate, $\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_3.6\text{H}_2\text{O}$.

	Found.	Calculated.
Sb	30.58 30.76	30.30
C	18.14	18.18
H	3.01	3.03
Water at 160°	13.86	13.63

This salt is easily soluble in water. In its cold solution sodium carbonate produces no turbidity; but, upon heating, a copious white precipitate is thrown down. This particular precipitate we did not examine more closely, but its nature may be inferred from evidence to be cited later. It undoubtedly consists either of basic mixtures or of antimonious oxide, according to the amount of sodium carbonate used and the thoroughness of the boiling.

Attempts were made to prepare definite salts of antimonio-tritartaric acid, but unsuccessfully. Barium carbonate dissolves in a solution of the acid with brisk effervescence, but, upon standing, crystals of ordinary barium tartrate were deposited. The anti-

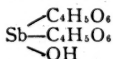
mony in this case remained dissolved undoubtedly as the normal tritartrate. In another experiment a solution of the acid was rapidly neutralised with barium carbonate, and subsequently precipitated by alcohol. The copious white precipitate was washed with alcohol, air dried, and partially analysed. So far as ascertained its composition agrees with the formula $\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 4\text{BaC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$. It is probably a mixture.

	Found.		Calculated.
Sb	12.47		12.77
Ba	28.27	29.06	29.17
Water at 150°	2.45		2.87

Second. It has already been stated that a saturated solution of antimonious oxide in tartaric acid does not crystallise. Such a solution (marked 1 in the previous table) was evaporated to dryness and the dry product was analysed. The results were as follows:

Sb	27.53
C	18.31
H	2.96
H ₂ O at 105°	10.92

This analysis is of dubious value. The compound may not have been definite, and the figures agree sharply with no probable formula. The antimony and carbon give a ratio corresponding to seven molecules of acid to four atoms of metal, and suggest the existence of a compound having the formula $\text{Sb}(\text{OH})\text{H}_2(\text{C}_4\text{H}_4\text{O}_6)_7$. Such a formula, which may be written structurally



is also indicated by Peligot's analysis of his "hyperacid tartrate," but it is not clearly proved. It is also further suggested by the following reaction:

A solution containing the foregoing salt was mixed with alcohol. The usual white precipitate was washed with alcohol and air-dried over sulphuric acid. Its composition is clearly represented by the formula $\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_3 \cdot 0.6\text{H}_2\text{O}$.

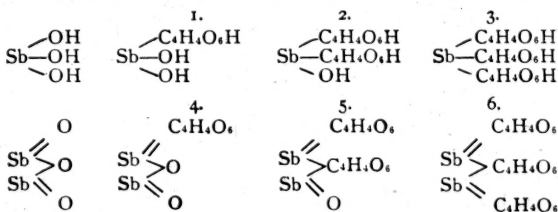
		Found.		Calculated.
Sb	36.88	36.22	36.58	36.37
C	13.56	13.90	13.56	14.54
H	2.65	2.72	2.47	3.03
H ₂ O at 155°	16.31	...	...	16.36

A portion of this was redissolved in water, and the solution was left to evaporate. No crystals formed, but the liquid dried up to a yellowish, scaly mass, containing 16.39 per cent. of water. Evidently no change in composition had occurred. Heated to 170° the salt lost another molecule of water, leaving two molecules of $\text{Sb} \equiv \text{C}_4\text{H}_3\text{O}_4$.

Actual loss at 170° , 19.28 per cent. Theoretical, 19.09.

A similar precipitate was also examined by Peligot, who dried his product at 160° and estimated only carbon and hydrogen. From his results the formula $\text{SbC}_4\text{H}_3\text{O}_4$ has been inferred, as well as the existence of an acid salt $\text{SbC}_4\text{H}_3\text{O}_7$.¹ The latter compound, however, he never actually obtained; and the only evidence of its existence and properties was published from this laboratory some four years ago.²

If now we compare the formulæ of our two acid salts (using our hypothetical formula for the second) with those of the two alcoholic precipitates, certain obvious relations will appear. There ought plainly to be two series of antimony tartrates, one acid and one neutral; the first derived from orthoantimonious acid, $\text{Sb}(\text{OH})_3$, and the other from antimonious oxide, Sb_2O_3 . The formulæ should be as follows, neglecting water of crystallization:



Of these, numbers 3, 5 and 6 we have actually obtained in definite condition, and number 2 we have shown to be probable. The latter is related to the neutral ditartrate just as antimonio-tritartaric acid is related to the tritartrate, and the name of antimonio-ditartronic acid may fitly be applied to it. By precipitation with alcohol it yields a neutral ditartrate, precisely as number 3 by a similar reaction yields number 6. The formula, doubled, and with five molecules of water added, is found in all reference works upon chemistry as that of Peligot's hyperacid tartrate.

¹ Commonly written $\text{C}_4\text{H}_3\text{H}(\text{SbO})\text{O}_4$.

² Clarke and Stallo, this Journal, 2, 319.

The hypothetical compound numbered 1 in the foregoing schedule we did not obtain. Number 4, the monotartrate, we attempted to investigate, but with only partial success. After a number of failures, which resulted in the formation of the neutral ditartrate, we prepared a quantity of antimonious hydroxide, which we dissolved to saturation in aqueous tartaric acid. This solution yielded a precipitate with alcohol which was comparatively insoluble in water, and which, air-dried, had the subjoined composition:

	Found.		Calculated for $\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2\text{O}_2 \cdot 2\text{H}_2\text{O}$.
Sb	53.62	53.84	52.63
C	6.43	5.38	10.52
H	1.65	1.51	1.75
H_2O at 160°		7.79	7.89

It will at once be seen that the analysis, though suggestive, is highly unsatisfactory. It merely emphasises the probability that the compound sought for exists. The white precipitate described by Berzelius had similar properties as regards insolubility, and his formula for it, translated into modern notation, agrees with ours. On the antimonyl hypothesis its formula is found in works of reference as $\text{C}_4\text{H}_4(\text{SbO})_2\text{O}_6$. It needs, however, further investigation.

In all essential particulars the salt which we call antimonio-ditartaric acid behaves much like the corresponding tri-compound. It is strongly acid, effervesces with carbonates, and is not precipitated by alkalis in the cold. Its solution, saturated with barium carbonate and precipitated by alcohol, behaved precisely like that of the tri-acid, but the curdy white precipitate had a different composition. A partial analysis gave results agreeing with $\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2\text{O}_2 \cdot 3\text{BaC}_4\text{H}_4\text{O}_6 \cdot 11\text{H}_2\text{O}$.

	Found.		Calculated.
Sb	15.33		14.94
Ba	26.06	26.63	25.58
H_2O at 150°	12.66		12.32

This too is most probably a mixture, although both it and the corresponding tri-acid precipitate may be weak double compounds.

In order to get further evidence concerning the nature of the acid compounds, we neutralised a solution of the di-acid with sodium carbonate. The liquid, which remained perfectly clear,

was then mixed with alcohol. At first it became turbid, and later it separated into two fluid layers, both clear, and both containing antimony. The lower layer was syrupy, and contained most of the sodium; it was accordingly drawn off, and evaporated at the ordinary temperature of the air over sulphuric acid. It slowly dried up to an amorphous, gummy mass, which yielded a yellowish powder. This product we analysed. Although, under the circumstances, we could hardly expect a definite compound, our figures approximate to what is required by the empirical formula, $2\text{Sb}(\text{OH})_3 \cdot 3\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$.

	Found.		Calculated.
Sb	24.66	25.00	24.54
Na	13.48		14.11
C	15.64	15.77	14.72
H	2.62		2.45
H ₂ O at 150°	11.66		11.04

This compound is probably definite, although we may have failed to determine exactly the right formula. It is readily soluble in water, and very faintly acid towards litmus paper. Its solution is stable even upon boiling, but is precipitated, when hot, by alkaline carbonates.

Another portion of the antimonio-ditartaric acid solution was exactly neutralised by sodium carbonate and boiled. A heavy precipitate fell, which we collected and dried over sulphuric acid. To the filtrate more sodium carbonate was added, and a second boiling threw down a second precipitate. Both precipitates, 1 and 2, were analysed.

	I.		II.
Sb	47.87	47.28	84.25
C	3.96	4.24	...
H	3.44	3.21	...
H ₂ O, 155°	22.30		4.80

The second product is evidently antimonious oxide mixed with a little hydrate. The pure oxide contains 83.33 per cent. of metal. The first precipitate approximates roughly to a tartrate having the formula $\text{Sb}_2\text{O}_3(\text{C}_4\text{H}_4\text{O}_6) \cdot 12\text{H}_2\text{O}$, analogous to the sulphate $\text{Sb}_2\text{O}_3(\text{SO}_4)$, the chloride $\text{Sb}_2\text{O}_3\text{Cl}_3$, etc. Doubtless such a tartrate exists, and might be prepared in a state of purity by proper precautions. It should contain 51.95 per cent. Sb, 5.20 per cent. C,

3.03 per cent. H, 23.37 per cent. H_2O . Our results, however, only indicate the probability of such a basic salt, formed by the partial precipitation of the higher tartrates, as a step in the reduction of the latter to oxide.

With the neutral¹ ditartrate of antimony one more suggestive experiment was tried. Its solution was cautiously mixed with dilute sulphuric acid to incipient turbidity, and then immediately precipitated by alcohol. The precipitate, which was white, contained sulphuric and tartaric acids, antimony and water.

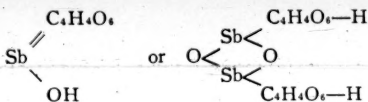
	Found.	
Sb	33.56	
SO_4	25.48	25.52
H_2O at 110°	12.31	

A compound having the formula $Sb_2(C_4H_4O_6)(SO_4)_{1.7}H_2O$, would require 33.99 per cent. Sb, 27.19 per cent. SO_4 , and 17.84 per cent. H_2O . A loss of $5H_2O$ would amount to 12.75 per cent. Our figures, however, here as in several other cases, are merely sufficient to establish a probability which may serve as a basis for future investigations. It may be regarded as practically certain that mixed salts of antimony are possible, and that sulphato-tartrates, etc., may be obtained by careful and systematic trial. Want of time precluded us from working farther in this direction.

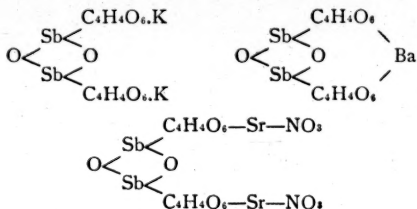
The foregoing results, taken altogether, establish certain points pretty clearly. First, contrary to Peligot's views, antimony forms perfectly normal tartrates, in which it acts like any other trivalent metal, and in which the assumption of an antimonyl radicle, SbO , is entirely inadmissible. The other tartrates of antimony fall naturally into series, in which we sometimes find the atoms Sb and O united in accordance with Peligot's hypothesis, but not in such a way as to give the latter any validity. In all such cases the SbO group is not to be regarded as a distinct radicle, but rather as an incident in a series; a mode of union found in many other basic compounds of other metals for which no special explanation has ever been thought necessary. In the tartar emetics we have a set of salts which may or may not be interpreted on the antimonyl theory, as was shown in this laboratory some years ago, but which are best explained by regarding them as derived from a complex

¹ The word "neutral" is inexact, but serves provisionally to indicate those tartrates of antimony which contain no replaceable hydrogen. Some of them are really basic.

tartrantimonious acid, to which may be assigned either of the two formulæ given below :



The first formula was adopted in the paper from this laboratory which we previously cited, but the latter is suggested by the fact that tartar emetic, as usually written, contains only half a molecule of water, and that therefore its formula should be doubled. On this plan the tartar emetics of barium and potassium may be formulated as below, and Kessler's double salt of strontium tartar emetic and strontium nitrate becomes easily explainable also.



In the course of our present investigation we have done some work upon this class of compounds, and notably as follows: A quantity of silver tartar emetic was dissolved in boiling water and precipitated by the addition of amyl iodide. Silver iodide was thrown down, the solution was instantly filtered, and upon cooling white brilliant crystals were deposited. These were insoluble in water and too small for us to determine their form. Analysis gave a composition best represented by the empirical formula $2\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2.\text{Ag}_2\text{C}_4\text{H}_4\text{O}_6.3\text{H}_2\text{O}$.

	Found.		Calculated.
Sb	37.37	38.54	38.15
Ag		17.19	17.17
C	11.21	11.26	11.45
H	1.15	1.21	1.42
H ₂ O, at 150°		3.43	4.29

Although the agreement here is very close, and the preparation of the salt, repeated several times, gave a perfectly uniform and apparently definite product, the formula cannot be regarded as certain. Our difficulty is that a similar experiment with ethyl iodide gave a salt of similar appearance but of different composition, as follows :

Sb	33.37
Ag	21.61
C	11.86
H	1.16
H ₂ O	4.44

Possibly this preparation, which we made only once, contained unaltered silver tartar emetic. At all events, uncertainty exists, and further investigation is necessary. If the formula given above should prove to be correct it would relate the compound structurally to the salts $\text{Sb}_2\text{O}_3\text{Cl}_2$, $\text{Sb}_2\text{O}_3(\text{SO}_4)$, etc.

In conclusion, we may describe the following new tartrantimonites :

Aniline tartrantimonite, $\text{SbC}_4\text{H}_5\text{O}_7\cdot\text{C}_6\text{H}_7\text{N}$, was obtained by treating the barium salt with a solution of aniline sulphate. It crystallises very easily in long white prisms, sometimes discolored by traces of oxidation products, and has a specific gravity of 1.890 at 11°. It yielded 31.74 per cent. of antimony, which is exactly the theoretical amount.

The quinine and atropine tartar emetics were prepared in a similar manner by Mr. Karl W. Langenbeck. Both salts were amorphous, yellowish, translucent masses. The quinine salt was anhydrous ; the atropine salt contained two molecules of water. The analytical data are subjoined :

Quinine Salt.	Found.		Calculated.
Sb	19.63	19.76	19.70
Atropine Salt.	Found.		Calculated.
Sb	19.88		19.67
H ₂ O	5.62		5.90

Contributions from the Chemical Laboratory of Harvard College.¹

XXXI.—ON CERTAIN SUBSTITUTED ACRYLIC AND PROPIONIC ACIDS.

By C. F. MABERY AND F. C. ROBINSON.

β -dibromacrylic acid, unlike the isomeric α -acid, will not unite with bromine at ordinary temperatures. After standing twelve days, a solution of the acid with bromine in chloroform was not bleached, and by slow evaporation of the solution, crystals were deposited which melted at 86° , the melting point of dibromacrylic acid. At 100° the addition of bromine was easily accomplished. When pure dibromacrylic acid was heated in a closed tube with undiluted bromine in slight excess over the calculated amount, for one or two hours, tetrabrompropionic acid was formed in nearly the theoretical quantity. The excess of bromine was removed by evaporation from the crude product, which was purified by pressure in filter-paper and crystallisation from carbonic disulphide and chloroform. From a concentrated solution in carbonic disulphide it crystallises by slow evaporation in oblique prisms. It is somewhat soluble in hot water, from which it separates at first as an oil; but on further cooling it crystallises in thick prisms. On boiling an aqueous solution of the acid it is rapidly decomposed, imparting a milky appearance to the solution, probably from the formation of tri-bromethylen. Melting point 118° – 120° . Its composition was determined by the following analyses.

I. 0.2149 gram of the substance gave by Carius' method 0.4169 gram AgBr.

II. 0.1639 gram of the substance gave 0.3145 gram AgBr.

III. 0.8899 gram of the substance gave 0.2857 gram CO_2 and 0.0478 gram H_2O .

Calculated for $\text{C}_3\text{H}_2\text{Br}_4\text{O}_2$.		Found.		
		I.	II.	III.
Br	82.04	82.55	81.76	
C	9.23			8.76
H	.51			.60

¹ The work contained in papers XXXI and XXXII was done in connection with the summer course of instruction in chemistry for 1882.—C. F. M.

The barium, calcium, and potassium salts of this acid were made and analysed. We were unable to prepare the silver salt in a form sufficiently pure for analysis. Argentic bromide began to separate even in the dark as soon as the salt was formed.

Baric tetrabrompropionate, $\text{Ba}(\text{C}_3\text{HBr}_4\text{O}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$? To prepare this salt, a solution of the acid was saturated with baric carbonate, filtered, and allowed to evaporate spontaneously at the ordinary temperature.

From the concentrated solution the salt crystallised in flat prisms, which were very soluble in water. In aqueous solution the salt is permanent when exposed to the air at ordinary temperatures, but it is rapidly decomposed by heat. In the following determinations of the water of crystallisation, in each case the salt was dried to a constant weight in the air and then heated until constant at 80° .

- I. 1.2784 grams of the air-dried salt lost 0.0090 gram H_2O at 80° .
- II. 1.0862 grams of the air-dried salt lost 0.0081 gram H_2O at 80° .
- III. 1.2403 grams of the air-dried salt lost 0.0087 gram H_2O at 80° .

Calculated for $\text{Ba}(\text{C}_3\text{HBr}_4\text{O}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$.		Found.		
		I.	II.	III.
H_2O	.96	.7	.7	.75

1.0762 grams of the salt dried at 80° gave 0.2747 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_3\text{HBr}_4\text{O}_3)_2$.	Found.
Ba	14.97	15.01

Calcium tetrabrompropionate, $\text{Ca}(\text{C}_3\text{HBr}_4\text{O}_3)_2 \cdot \text{H}_2\text{O}$. When an aqueous solution of the acid was neutralised with calcic carbonate in the cold and evaporated at the ordinary temperature, the calcium salt separated from the concentrated solution in clusters of microscopic prisms, which were much less soluble in water than the corresponding barium salt. The air-dried salt contained one molecule of water of crystallisation, which was given up at 80° .

- I. 1.1413 grams of the air-dried salt gave 0.0215 gram H_2O at 80° .
- II. 1.1087 grams of the air-dried salt gave 0.0205 gram H_2O at 80° .
- III. 1.0948 grams of the anhydrous salt gave on ignition with H_2SO_4 0.1895 gram CaSO_4 .

Calculated for $\text{Ca}(\text{C}_3\text{HBr}_4\text{O}_2)_2 \cdot \text{H}_2\text{O}$.		Found.	
		I.	II.
H ₂ O	2.15	1.88	1.85
Calculated for $\text{Ca}(\text{C}_3\text{HBr}_4\text{O}_2)_2$.		Found.	
Ca	4.89	5.09	

Potassic tetrabrompropionate, $\text{KC}_3\text{HBr}_4\text{O}_2 \cdot 2\text{H}_2\text{O}$. By the action of an aqueous solution of potassic carbonate on the acid a neutral solution was obtained, from which by spontaneous evaporation the potassium salt was deposited in the form of clustered needles. This salt is very soluble in water and permanent in the air at ordinary temperatures, but rapidly decomposed by heat. The air-dried salt gave up its water of crystallisation over sulphuric acid.

I. 1.1571 grams of the air-dried salt lost over H_2SO_4 0.0882 gram H_2O .

II. 1.1304 grams of the air-dried salt lost over H_2SO_4 0.0858 gram H_2O .

III. 1.0354 grams of the anhydrous salt gave on ignition with H_2SO_4 0.2165 gram K_2SO_4 .

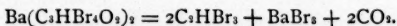
Calculated for $\text{KC}_3\text{HBr}_4\text{O}_2 \cdot 2\text{H}_2\text{O}$.		Found.	
		I.	II.
H ₂ O	7.76	7.62	7.59
Calculated for $\text{KC}_3\text{HBr}_4\text{O}_2$.		Found.	
K	9.14	9.39	

When heated in aqueous solution the barium salt was easily decomposed with the separation of an oil which distilled readily with steam. Since tribromethylen was the only substituted hydrocarbon that could be derived from tetrabrompropionic acid under these conditions, it was converted directly into pentabromethan. The salt was distilled with an excess of baric hydrate, and the oily distillate absorbed by bromine water. A solid residue was left after evaporation of the excess of bromine, which melted at 53° when purified by crystallisation from alcohol, and on analysis gave the required percentage of bromine.

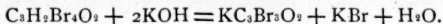
0.0918 gram of the substance gave 0.2041 gram AgBr .

	Calculated for C_3HBr_3 .	Found.
Br	94.12	94.61

Carbonic dioxide was evolved in this decomposition, and the retort residue contained baric bromide in large quantity. It may therefore be expressed by the following equation:



On standing with an alcoholic solution of potassic hydrate, a molecule of hydrobromic acid was eliminated from the acid with the formation of tribromacrylic acid, according to the equation:



Tribromacrylic acid was recognised by its melting point, 118° , and by its crystalline form.

If the structure of β -dibromacrylic acid¹ is represented by the formula,



the bromine addition-product would have the form,



The above statement concerning the behavior of β -dibromacrylic acid towards bromine holds true with regard to chlorine. Although no action takes place at ordinary temperatures, when chlorine is passed through the melted acid the addition-product is formed without difficulty. The resulting dichlorodibromopropionic acid will be submitted to further examination.

We have also tried the action of hydrobromic acid upon β -dibromacrylic acid, but as yet our results are as unsatisfactory as those of Fittig and Petri.² The product melted at about 53° and gave a percentage of bromine which showed that it contained much unaltered dibromacrylic acid. Nevertheless, by prolonged heating, we hope to obtain the tribromopropionic acid in a form sufficiently pure to enable us to study its properties.

Several attempts were made to obtain an addition-product by the action of bromine monochloride on bromopropionic acid. A substance was formed which melted quite constant at 110° - 112° ; but the results of analyses indicated that it was a mixture of the chlorine and bromine addition-products. In one experiment a

¹ H. B. Hill. This Journal, **4**, 276, and Proceedings American Academy, **17**, 153.

² Annalen der Chemie, **195**, 73.

product was obtained which melted at 102° – 105° , and the percentage of bromine was very considerably increased. There is little doubt that the addition would take place, provided the bromine monochloride could be obtained in a state of purity under conditions necessary to form addition-products.

When brompropionic acid is dissolved in chloroform saturated at 0° with chlorine, and allowed to stand for some time, the chlorine is absorbed with the formation of bromdichloracrylic acid.

XXXII.—ON THE DECOMPOSITION OF CHLORTRIBROMPROPIONIC ACID BY ALKALINE HYDRATES.

By C. F. MABERY.

In a previous paper by H. C. Weber and myself,¹ some experiments were mentioned in which we had attempted to determine the decomposition-products of chlortribrompropionic acid. Although our results were not entirely satisfactory, we were unable to verify them on account of the limited time at our disposal. Since the necessary material could be obtained without difficulty, it seemed worth while to define this reaction with greater precision. This work was undertaken by Mr. R. D. Wilson, who found that on prolonged heating with baric hydrate in aqueous solution, chlortribrompropionic acid was completely decomposed, according to the equation,



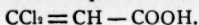
For identification the volatile product of the distillation was converted into chlortetrabromethan. It was caught in bromine water, the excess of bromine allowed to evaporate, and the oil which separated cooled to 0° . The solid thus obtained was purified by crystallisation from alcohol, and its composition determined by analysis.

0.1556 gram of the substance gave 0.3657 gram $\text{AgBr} + \text{AgCl}$.

	Calculated for C_2HClBr_2 .	Found.
$\text{Cl} + 4\text{Br}$	93.42	93.30

¹ This Journal, 4, 106, and Proceedings American Academy, 17, 209.

Since this substance melted at 33° , it was probably identical with the chlortetrabromethan, melting point 32° – 33° , obtained by Wallach and Bischof,¹ from the decomposition of β -dichloracrylic acid.



This acid gave chloracetylen, $\text{CCl} \equiv \text{CH}$, which by the addition of bromine formed chlortetrabromethan,



By the action of potassic hydrate in alcoholic solution upon chlortribrompropionic acid, the elements of hydrochloric acid were eliminated, with the formation in small quantity of tribromacrylic acid.

From the evident analogy between chlorbromacrylic acid, from which chlortribrompropionic was made, and β -dibromacrylic acid, the structure of chlorbromacrylic acid² is probably,



Chlortribrompropionic acid would then have the form,



XXXIII.—ON THE PRODUCTS OF THE DRY DISTILLATION OF WOOD AT LOW TEMPERATURES.

BY CHARLES F. MABERY.

In the manufacture of acetic acid by the dry distillation of wood at low temperatures, as it is conducted by Dr. E. R. Squibb, of Brooklyn, N. Y., an oil heavier than water collects during the distillation in considerable quantities. Upon examination, Professor H. B. Hill³ found that this oil contained a large percentage of furfural, and that by the action of alkalies upon it a small quantity

¹ *Annalen der Chemie*, **203**, 89.

² H. B. Hill, this Journal, **4**, 276; and *Proceedings American Academy*, **17**, 153.

³ This Journal, **3**, 33; and *Proceedings American Academy*, **16**, 102.

of pyroxanthin was formed. Further information concerning the more volatile products of the distillation therefore seemed desirable; and since different portions of the crude methyl alcohol were kindly placed at my disposal by Dr. Squibb, I undertook an examination of its constituents.

The composition of crude wood spirit has frequently been made the subject of investigation within a few years. Beside methyl alcohol and methyl acetate, which constitute the greater part of the product in the ordinary process of distillation, acetic aldehyde, acetic acid, acetone, acetal, dimethylacetal, methylethylketone, and allyl alcohol have been found in smaller quantities. Traces of the higher ketones have been detected in the less volatile portions, and in the high boiling oils small quantities of the aromatic hydrocarbons toluol, xylol, and cumol.

A study of the product under consideration shows that it has essentially the same composition. Its distinctive characteristic consists in different quantitative proportions of several constituents, probably due to the low temperature at which the first distillation was conducted. It also contains methyl formate, which has not hitherto been recognised as a constituent of wood spirit.¹

Three portions were selected for examination. The first portion (*a*) was collected at the beginning of the distillation, the second (*b*) after several hundred gallons had distilled, and the third (*c*) when the distillation of methyl alcohol was well advanced. Each portion was bright yellow in color, and from (*a*) and (*b*) a sharp penetrating odor was emitted. Since various attempts to remove the small percentage of water by desiccation were unsuccessful, the product was fractional as it was received. Anhydrous cupric sulphate absorbed only a small fraction of the water, even after standing several weeks, and fused potassic carbonate produced a decomposition, as shown by the color changing to a dark brown, with the formation of a yellow precipitate on standing. In the fractional distillation very satisfactory results were obtained, both in the separation of the different fractions and in economy of time, by the use of Hempel's² device for condensation.

The following table contains the results of the tenth fraction of each portion expressed in percentages. To insure a more com-

¹ Krämer and Grodzky succeeded in isolating formic acid in small quantity from the oil obtained by adding sulphuric acid to the mother liquor of *Holzessig*, after removing the greater part of the acetic acid as sodic acetate. (*Berichte der deutschen chemischen Gesellschaft*, **11**, 1356.)

² *Zeitschrift für analytische Chemie*, **20**, 508.

plete condensation of the volatile products in (a), after passing through a Liebig's condenser, the distillate was cooled by a freezing mixture. Considerable gas escaped condensation at the beginning of the distillation, but it was found to consist chiefly of carbonic dioxide.

The residue of the distillation in each case contained the greater part of the water, though in (a) it consisted chiefly of methyl alcohol. In (b) approximately one-half of the residue consisted of the higher boiling oils, and in (c) it was composed beside water of furfural and an oil of low specific gravity. The constituents of the various fractions will be described in detail.

(a)		(b)		(c)	
Temperatures.	Percentages.	Temperatures.	Percentages.	Temperatures.	Percentages.
20°-25°	2.1				
25-30	1.5				
30-40	1.				
40-50	1.				
50-52	1.6				
52-54	9.3	Below 54°	3.		
54-56	62.8		74.1		
56-60	7.3		3.6	Below 63°	4.7
Above 60°	6.7	60°-70°	3.7	63°-65°	2.5
		Above 70°	9.9	65°-68°	57.9
				Above 68°	31.4
Loss	6.7		5.7		3.5

Acetic Aldehyde.

In (a) the fraction that came over between 20° and 25° was very soluble in water, and it gave the penetrating odor characteristic of acetic aldehyde. This substance was also recognised in that portion of (b) which distilled below 54°, and in the fraction below 63° in (c). It formed a compound with acid sodic sulphite, crystallising in flat prisms, which were very soluble in water. In order to establish its identity, an aqueous solution of the fraction 20°-25° was boiled with an excess of silver oxide, filtered, and concentrated by evaporation. On cooling, silver acetate crystallised in characteristic forms, which, on analysis, gave the required percentage of silver.

I. 0.2222 gram of the substance gave on ignition 0.1432 gram Ag.

II. 0.3167 gram of the substance gave on ignition 0.2050 gram Ag.

Calculated for $\text{AgC}_2\text{H}_3\text{O}_2$.		Found.	
		I.	II.
Ag	64.68	64.43	64.73

According to Krämer and Grodzky,¹ in the manufacture of wood spirit, acetic aldehyde may usually be found in the first portions of the distillate. It is rarely present in large quantities, since, as they assert, the greater part is converted into dimethylacetal during the distillation.

Methyl Formiate.

This substance was isolated from the fractions 25°–30° and 30°–40°. On the addition of water an oil separated, which was purified by fractional distillation. There were thus obtained 8 grams of a substance which distilled between 30° and 35°. It was saponified by boiling with an excess of plumbic hydrate, and the composition of the plumbic formiate determined by analysis.

I. 0.5214 gram of the substance dried over H_2SO_4 gave on ignition with H_2SO_4 0.5296 gram PbSO_4 .

II. 0.2900 gram of the substance gave 0.2960 gram PbSO_4 .

Calculated for $\text{Pb}(\text{CHO}_2)_2$.		Found.	
		I.	II.
Pb	69.69	69.42	69.71

The presence of formic acid, and the quantity of the distillate which collected between 40°–50°, suggested the possible formation of methylal. This fraction was therefore treated with an equal volume of water, and the oil which separated boiled with plumbic hydrate to decompose the methyl formiate. After drying with fused calcic chloride, the residue distilled above 50°. In another attempt to isolate methylal, 2000 grams of (a) were fractioned, and the distillate below 50° examined according to Dancer's method² for the separation of dimethylacetal. As in the first experiment, the residue distilled at a temperature far above the boiling point of methylal, which seemed to indicate that this substance could not have been formed in any appreciable quantity.

¹ Berichte der deutschen chemischen Gesellschaft, 9, 1920.

² Annalen der Chemie, 132, 240.

Methyl Acetate.

Since the fractions 50° – 52° and 52° – 54° gave reactions for aldehyde and acetone, they were evidently a mixture of these substances with methyl acetate. The greater part of the methyl acetate in (a) and (b) was collected in the fraction 54° – 56° , which boiled constant at 54.5° – 55.5° (Bar. 769.5 mm.). To determine approximately the percentage of methyl alcohol in this fraction, 655 grams were saponified with potassic hydrate, and distilled. After drying with fused potassic carbonate and distilling off the methyl alcohol, there were obtained 255 grams, which came over between 66° and 67° (Bar. 769.5 mm.), or 92 per cent. of the amount required from the weight taken of methyl acetate. In repeating this saponification in a dilute solution of methyl acetate, with a potassic hydrate solution of known strength, the excess of alkali was titrated with standard sulphuric acid, and the percentage of methyl acetate calculated from the amount of potassic hydrate required to decompose it. This method gave 99.2 per cent. of pure methyl acetate.

Methyl Alcohol.

Although a small amount of methyl alcohol was contained in the higher fractions of (a) and (b), it was evidently condensed for the most part in the fraction 65° – 68° of (c). This fraction was slightly yellow in color, but no further attempts were made to determine its purity than an estimation of the percentage of acetone, which will presently be described.

Dimethylacetal.

The formation of dimethylacetal during the dry distillation of wood for the preparation of methyl alcohol was not observed until 1864, probably because of the small difference between its boiling point (64°) and that of methyl alcohol. After removing the methyl alcohol and acetone, Dancer¹ succeeded in separating a product which proved to be identical with dimethylacetal, made by heating methyl alcohol with acetic aldehyde. Krämer and Grodzky² state that it has since been recognised as a constant constituent of wood spirit. Its formation is probably due to the high temperature of

¹ *Annalen der Chemie*, **132**, 240.

² *Berichte der deutschen chemischen Gesellschaft*, **9**, 1920.

the distillation, which enables the aldehyde to act upon the methyl alcohol. From the large percentage of aldehyde in the product under consideration, it would seem that this reaction had not taken place to any extent. Since an examination of the distillate below 65° in (c) failed to reveal the presence of dimethylacetal, a second portion of 2000 grams was fractioned, the lower fraction saponified and distilled over calcic oxide. The small amount of residue left after removing the methyl alcohol with calcic chloride, distilled at 57°-58°, was readily miscible with water, and its reactions in general were characteristic of acetone. Dimethylacetal could not therefore have been formed in quantity sufficient for identification.

Acetone.

The first quantitative experiments on the influence of acetone upon the commercial value of methyl alcohol were made by Krämer and Grodzky.¹ They determined the quantity of dimethylaniline which could be obtained from a given weight of pure methyl alcohol, and also from methyl alcohol containing different amounts of acetone. Their results seemed to show that the yield was very considerably diminished if the quantity of acetone exceeded one per cent. Since crude wood spirit always contains a much higher percentage, it must be specially purified for the preparation of dimethylaniline.

Various methods, dependent either upon the physical or chemical properties of methyl alcohol, have been proposed for testing its purity. Krell² suggested a determination of the amount of methyl iodide which could be obtained by treating a given quantity of the alcohol with phosphorous iodide. In the hands of a skilful analyst the percentage of methyl alcohol may be accurately determined by this method; but, as Krämer remarked, it does not account for the nature of the impurities, and it is not sufficiently expeditious. To overcome these objections, Krämer³ took advantage of the formation of iodoform from acetone. In his modification of Lieben's reaction⁴ the formation of iodoform from ethyl alcohol and acetic acid is avoided, and acetic aldehyde is only partially decomposed.

According to Krämer's method a mixture of 10 cc. of a normal sodic hydrate solution, 5 cc. of a double-normal iodine solution and 1 cc. of the alcohol to be tested is shaken in a graduated cylinder

¹ Berichte der deutschen chemischen Gesellschaft, 13, 1005.

² *Ibid.* 6, 1310.

³ *Ibid.* 13, 1000.

⁴ Annalen der Chemie, Suppl. VII., 218, 377.

with 10 cc. of ether. 5 cc. of the ether solution are withdrawn with a pipette, evaporated on a weighed watch-glass, and the residue weighed after drying in a warm desiccator. To obtain the weight of acetone in 1 cc. of the alcohol, the weight of iodoform is multiplied by .28 if there are 9.5 cc. of the ether solution.

The percentage of acetone in several fractions, as determined by this method, is giving in the following table.¹ Since in each determination from 9 cc. of the ether solution 5 cc. were evaporated, the weight of iodoform was multiplied by .27 for the weight of acetone.

Fraction treated.	Specific Gravity.	Weight of Iodoform.	Weight of Acetone.	Percentage of Acetone.
54°-56° (a)	0.935	0.0359	0.0097	1.04
Below 54° (b)	0.930	0.0648	0.0175	1.88
54°-56° (b)	0.935	0.0638	0.0182	1.95
Methyl Alcohol				
from 54°-56° (b)	0.805	0.0914	0.0247	3.07
56°-60° (b)	0.830	0.0802	0.0217	2.66
65°-68° (c)	0.820	0.1037	0.0280	3.41

Although the quantity of acetone in the product under consideration is sufficiently large to render further purification necessary, it is evidently much smaller than is usually observed in commercial wood spirit.

Allyl Alcohol.

The occurrence of allyl alcohol as a product of the distillation of wood was first mentioned by Aronheim,² and soon afterward Krämer and Grodzky³ stated that small quantities of it may always be found in the higher fractions. In examining the aqueous part of the residue in (c) for this substance, after removing the water, a small amount of an oil was left, with a boiling point somewhat higher than that of allyl alcohol. It absorbed bromine readily, with the formation of a product which boiled much too low for dibromallyl alcohol, and oxidation with nitric acid gave only oxalic acid. Since from the results of Krämer and Grodzky it is usually present in wood spirit, in quantity not exceeding two tenths of one

¹ In several instances the fraction was boiled with silver oxide before testing for acetone, but this seemed to have no appreciable effect on the quantity of acetone indicated by the iodoform reaction.

² *Berichte der deutschen chemischen Gesellschaft*, 7, 1381.

³ *Ibid.* 7, 1492.

per cent., it is evidently possible that the small amount contained in 2000 grams might escape observation.

High Boiling Oils.

Although the composition of the higher boiling fractions was not determined with sufficiently desirable accuracy, a brief description of my attempts to isolate substances which have already been found in the less volatile portions of wood spirit may have some interest. It has already been mentioned, that beside water these fractions consisted of an oil heavier and an oil lighter than water. The heavier oil was composed chiefly of furfural, though, as well as the water and lighter oil, it contained pyroxanthine in small quantity, which could be precipitated by the addition of sodic hydrate. 2000 grams of (c) gave 45 grams of the lighter oil, which was pale yellow when freshly distilled, but it turned dark brown on standing. In attempting to fraction it, a constant boiling point could not be obtained between 75° and 200°. About two grams of a substance distilled between 75° and 85°, which formed crystals with acid sodic sulphite, indicating the presence of methylethylketone; but the quantity obtained was insufficient for analysis. The penetrating odor observed in the distillate between 95° and 105° was characteristic of the allyl compounds. It was possibly due to a trace of allyl acetate, since after heating with sodic hydrate and neutralising the solution a qualitative test for acetic acid was obtained with ferric chloride. This oil distilled for the most part between 150° and 200°. Finding, however, that a constant boiling point could not be obtained with the supply of substance at my command, I did not consider it worth while to fraction the amount of material necessary to obtain the oil in large quantity.

The important characters of this product, as they have appeared in the course of the preceding examination, may be summarised as follows:

1. The high percentage of aldehyde in (a), of methyl acetate in (a) and (b), and of methyl alcohol in (c).
2. Presence of methyl formiate.
3. Absence of dimethylacetal.
4. Small percentage of acetone.
5. General purity of the product.

XXXIV.—RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

TWELFTH PAPER.

CERTAIN PARABROMBENZYL COMPOUNDS.¹

BY C. LORING JACKSON AND G. T. HARTSHORN.

In a previous paper of this series a number of parachlorbenzyl compounds containing sulphur were described; the following paper contains a description of the corresponding compounds made from the parabrombenzylbromide.²

Parabrombenzylsulpho-acid, $C_6H_4BrCH_2SO_3H$.

The potassium salt of this substance was made by heating parabrombenzylbromide with an aqueous solution of neutral potassic sulphite in a flask with a return-cooler until the odor of the bromide disappeared. It was purified by crystallisation from water, and dried first *in vacuo*, and afterwards at 110° , which showed that it contained no water of crystallisation.

0.2230 gram of the substance gave, according to Carius, 0.1454 gram of argentic bromide.

0.2624 gram gave 0.1724 gram of argentic bromide, and 0.2140 gram of baric sulphate.

0.2224 gram, after evaporation with sulphuric acid, gave 0.0688 gram of potassic sulphate.

	Calculated for $C_6H_4BrSO_3K$.	Found.	
Bromine	27.67	27.75	27.96
Sulphur	11.07		11.20
Potassium	13.50		13.89

It crystallises in narrow plates, which not infrequently reach a length of over one centimeter, and are characterised by a well-marked cleavage at right angles to their longer axis. On one occasion rhombic forms similar to those of the sodium salt of the parachlorbenzylsulpho-acid were observed. It is not freely soluble in cold water or alcohol, but its solubility in each of these solvents

¹ Presented to the American Academy. Communicated by the Authors.

² The results obtained will be found in tabular form at the end of the article.

is much increased by heat. The solubility in water at 18° was determined as follows :

I. 3.2760 grams of the saturated solution gave 0.2016 gram of the salt.

II. 2.7104 grams gave 0.1689 gram of the salt.

Percentage of $C_6H_4BrCH_2SO_3K$ in aqueous solution saturated at 18° :

I.	II.
6.15	6.25

To make the other salts of the sulpho-acid, the crude potassium salt was treated with a small quantity of plumbic acetate, to free it from bromide and sulphite ; and, after filtering from the precipitate thus formed, the lead salt was thrown down by adding an excess of plumbic acetate, and purified by crystallisation from water. It was then suspended in water, and treated with sulphuretted hydrogen to convert it into the free acid, which was used in the preparation of the following salts.

The *Calcium Salt* $(C_6H_4BrCH_2SO_3)_2Ca$, made by warming the acid with calcic carbonate, and purified by crystallisation from water, was free from water of crystallisation.

0.4472 gram of the salt dried at 110° gave 0.1096 gram of calcic sulphate.

0.2870 gram gave 0.0715 gram of calcic sulphate.

	Calculated for $(C_6H_4BrSO_3)_2Ca$.	Found.
Calcium	7.41	7.21 7.33

The salt crystallises in long colorless plates, and is freely soluble in water.

The *Barium Salt* $(C_6H_4BrCH_2SO_3)_2BaH_2O$ was made from the acid with baric carbonate, and purified by crystallisation from water.

0.4300 gram of the salt dried *in vacuo* lost, when heated to 110°, 0.0124 gram of water.

0.4396 gram lost 0.0123 gram of water.

	Calculated for $(C_6H_4BrSO_3)_2BaH_2O$.	Found.
Water	2.75	2.88 2.80

0.1630 gram of dried salt gave 0.0592 gram of baric sulphate.

0.3625 gram gave 0.1314 gram of baric sulphate.

	Calculated for $(C_6H_4BrSO_3)_2Ba$.	Found.
Barium	21.50	21.35 21.31

It crystallises in stellate groups of white needles, and is slightly deliquescent. Its solubility in water was determined as follows:

I. 4.0670 grams of the solution saturated at 18° gave 0.1649 gram of the salt.

II. 4.1510 grams gave 0.1679 gram of the salt.

Percentage of $(C_6H_4BrCH_2SO_3)_2Ba$ in aqueous solution saturated at 18° :

I.	II.
40.55	40.46

The *Lead Salt* $(C_6H_4BrCH_2SO_3)_2Pb$, made and purified as already described, was free from water of crystallisation.

0.3144 gram of the salt dried at 110° gave on combustion 0.2709 gram of carbonic dioxide, and 0.0481 gram of water.

0.2988 gram of the salt gave 0.1297 gram of plumbic sulphate.

	Calculated for $(C_6H_4BrSO_3)_2Pb$.	Found.
Carbon	23.76	23.51
Hydrogen	1.69	1.70
Lead	29.28	29.66

It crystallises in radiating groups of long white needles. Its solubility in water was determined as follows:

I. 4.3370 grams of the solution saturated at 18° gave 0.0873 gram of the salt.

II. 3.4536 grams gave 0.0691 gram of the salt.

Percentage of $(C_6H_4BrCH_2SO_3)_2Pb$ in aqueous solution saturated at 18° :

I.	II.
2.01	2.00

The *Chloride* of the *Sulpho-acid* $C_6H_4BrCH_2SO_3Cl$ was made by grinding the dry potassium salt in a mortar with phosphoric penta-chloride, and finishing the reaction by a gentle heat. The substance was precipitated on the addition of water as an oil, which solidified on standing, and was purified by crystallisation from ether or ligroine. It was dried *in vacuo* and analysed.

0.2460 gram of substance gave, by the method of Carius, 0.3000 gram of the mixture of argentic chloride and argentic bromide, and 0.2028 gram of baric sulphate.

	Calculated for $C_6H_4BrSO_3Cl$.	Found.
Chlorine and Bromine	42.85	42.50
Sulphur	11.87	11.35

It crystallises in small white prisms with a peculiar smell, similar to that of parabrombenzylbromide; but when cold it does not attack the mucous membrane, and when warmed only in a very much less degree than any of the brombenzylbromides. It melts at 115° , is essentially insoluble in water, and but slightly soluble in cold alcohol, ligroine, carbonic disulphide, and glacial acetic acid, freely soluble in all these solvents when hot, and in benzol and ether even in the cold.

Parabrombenzylsulphide, $(C_6H_4BrCH_2)_2S$.

This substance was made by boiling parabrombenzylbromide with an alcoholic solution of sodic sulphide; the reaction takes place very easily. The product obtained by distilling off part of the alcohol and precipitating with water was purified by crystallisation from alcohol. Dried *in vacuo* it gave the following results on analysis:

I. 0.1768 gram of substance gave, according to Carius, 0.1780 gram of argentic bromide.

II. 0.1807 gram gave 0.1828 gram of argentic bromide and 0.1057 gram of baric sulphate.

III. 0.2284 gram gave 0.1368 gram of baric sulphate.

	Calculated for $(C_6H_4Br)_2S$.	I.	Found. II.	III.
Bromine	43.01	42.85	43.06	...
Sulphur	8.60	...	8.04	8.23

Properties.—It crystallises in large thin plates, apparently rhombic crystals, which have a tendency to turn brown in the air; the odor is aromatic, and not especially disagreeable; it melts at 58° – 59° ; is essentially insoluble in water, soluble with difficulty in cold alcohol, ligroine, or glacial acetic acid, but freely in each of these solvents when hot, and in ether, benzol, or carbonic disulphide.

Parabrombenzylsulphone, $(C_6H_4BrCH_2)_2SO_2$, was made from the sulphide by dissolving it in glacial acetic acid, and adding the calculated amount of chromic anhydride also dissolved in glacial acetic acid. After the action had ceased, the substance was precipitated with water, and purified by crystallisation from alcohol. It was analysed after drying at 100° .

0.1674 gram of substance gave by the method of Carius 0.1556 gram of argentic bromide and 0.0991 gram of baric sulphate.

	Calculated for $(C_6H_4Br)_2SO_2$.	Found.
Bromine	39.60	39.56
Sulphur	7.92	8.13

It crystallises in white needles, with a slight not unpleasant smell; melts at 189° , and is essentially insoluble in water, soluble only to a slight extent in cold alcohol, benzol, ligroine, and glacial acetic acid, freely soluble in all these solvents when hot, and in ether and carbonic disulphide whether cold or hot.

Parabrombenzylmercaptan, $C_6H_4BrCH_2SH$.

This substance was made by the action of parabrombenzylbromide on an alcoholic solution of potassic sulphhydrate. The action took place very easily, and the product fell as an oil on the addition of water to the alcoholic solution. It was purified by distillation with steam, and solidified to a white crystalline mass after standing some time. It had a disagreeable odor, and melted at 25° , but we cannot be perfectly certain that this is the true melting point, on account of its strong tendency to pass into the disulphide on exposure to the air. The number given above, however, cannot be far from the correct one, as the sample was treated with zinc and sulphuric acid immediately before taking the melting point. It dissolves easily in all the common solvents with the exception of water and glacial acetic acid. It did not seem worth while to analyse the free mercaptan, as the results obtained from it are almost identical with those from its principal impurity, the disulphide; but instead of this, we determined its nature much more satisfactorily by converting it into the mercaptid, which was then analysed.

Parabrombenzylmercaptid, $(C_6H_4BrCH_2S)_2Hg$.

This substance was made by adding yellow mercuric oxide to the mercaptan suspended in water; after the action had ceased, the insoluble residue was purified by crystallisation from boiling alcohol, and dried at 100° .

0.2623 gram of substance gave on precipitation with sulphuretted hydrogen 0.1016 gram of mercuric sulphide.

Mercury

Calculated for $(C_6H_4BrS)_2Hg$.
33.11

Found.
33.38

It crystallises from boiling alcohol as a light white feathery mass with a pearly lustre. It does not melt, but is decomposed and blackened at a high temperature, is essentially insoluble in water, very slightly soluble in cold alcohol, benzol, or glacial acetic acid, freely soluble in hot alcohol (the solution becomes nearly solid on

cooling) and benzol, less so in hot glacial acetic acid, but freely in ether and carbonic disulphide.

Parabrombenzylsulphide, $(C_6H_4BrCH_2)_2S_2$.

This substance was made from the mercaptan by exposure to the air, and also by acting on the parabrombenzylbromide with an alcoholic solution of sodic disulphide; the product precipitated with water was purified by crystallisation from alcohol, and dried *in vacuo*.

0.1600 gram of the substance gave by the method of Carius 0.1487 gram of argentic bromide and 0.1838 gram of baric sulphate.

	Calculated for $(C_6H_4Br)_2S_2$.	Found.
Bromine	39.60	39.57
Sulphur	15.84	15.78

It crystallises in radiating groups of white needles, and has a not unpleasant aromatic smell; melting point, 87° – 88° . It is essentially insoluble in water, slightly soluble in cold alcohol, and almost insoluble in cold glacial acetic acid, but freely soluble in both these solvents when hot, and in ether, benzol, and carbonic disulphide.

The following table gives the formulas and melting points of the substances described in this paper.

Name.	Formula.	Melting point.
Parabrombenzylsulpho-acid		
Potassium Salt ¹	$C_6H_4BrCH_2SO_3K$	
Calcium Salt	$(C_6H_4BrCH_2SO_3)_2Ca$	
Barium Salt ²	$(C_6H_4BrCH_2SO_3)_2BaH_2O$	
Lead Salt ³	$(C_6H_4BrCH_2SO_3)_2Pb$	
Chloride	$C_6H_4BrCH_2SO_2Cl$	115°
Parabrombenzylsulphide	$(C_6H_4BrCH_2)_2S$	58° – 59°
Parabrombenzylsulphone	$(C_6H_4BrCH_2)_2SO_2$	189°
Parabrombenzylmercaptan	$C_6H_4BrCH_2SH$	25°
Parabrombenzylmercaptid	$(C_6H_4BrCH_2S)_2Hg$	
Parabrombenzylsulphide	$(C_6H_4BrCH_2)_2S_2$	87° – 88°

¹ The solution saturated at 18° contains 6.20 per cent of the salt.

² The solution saturated at 18° contains 40.50 per cent. of the salt.

³ The solution saturated at 18° contains 2.00 per cent. of the salt.

XXXV.—A NEW METHOD OF PREPARING BORNEOL FROM CAMPHOR.¹

BY C. LORING JACKSON AND A. E. MENKE.

The natural borneol (Borneo camphor), obtained from the *Dryobalanops Camphora*, is brought from the East so rarely that specimens of it can be obtained in this country or in Europe only with the greatest difficulty. Most chemists, who have studied this substance, have confined their attention therefore to the borneol obtained from ordinary camphor, which has been proved to be identical² with the natural product.

So far as we can find, there are but two methods of making borneol from camphor—one by the action of potassic hydrate, which is due to Berthelot;³ the other that of Baubigny,⁴ consisting in treating camphor with sodium, and separating the sodium camphor from the sodium borneol by carbonic dioxide. Both leave much to be desired, since the product of the first is a mixture of camphor and borneol, which must be purified by treatment with stearic acid, and according to Kachler⁵ the yield is very small, while the second yields pure borneol, it is true, but theoretically only one-half of the camphor can be converted into borneol, although an amount of sodium is required which corresponds to the whole weight of camphor used.

In the course of some experiments on camphor, which led to no result so far as their main object was concerned, it was necessary for us to become acquainted with the reduction of camphor; but, to our great surprise, we were unable to find any description of experiments on this subject, unless the statement in Beilstein's *Handbuch der organischen Chemie*, page 1763, that sodium amalgam does not act on camphor, comes under this head. We were compelled, therefore, to experiment ourselves, with the following result: 25 grams of camphor, melting at 175°, were dissolved in moist toluol, and sodium and water added at intervals, until a sample showed the melting point of borneol, 197°–198°; the toluol was then driven off by heat, and a yellowish white mass obtained,

¹ Presented to the American Academy. Communicated by the Authors.

² Kachler. Wien Acad. Ber. (2 Abth.). 78, July.

³ Annales de Chimie et de Physique, ser. 3, 56, 78.

⁴ Annalen der Chemie, 164, 75.

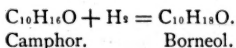
⁵ *Ibid.* ser. 4, 19, 221.

with the smell at once like camphor and pepper, described as that of borneol. It was purified by sublimation, and analysed with the following results:

0.1642 gram of substance gave 0.4700 gram of carbonic dioxide and 0.1772 gram of water.

	Calculated for $C_{10}H_{18}O$.	Found.
Carbon	77.93	78.07
Hydrogen	11.69	11.98

The substance is borneol, therefore, and the reduction of the camphor takes place, as was to be expected, according to the reaction,



The ease with which borneol was formed in this experiment led us to the following method for making borneol from camphor, which gives essentially the theoretical yield of nearly pure borneol with remarkably little trouble.

It consists in dissolving the camphor in about ten times its weight of common alcohol, and adding one-third¹ more than the amount of sodium calculated from the reaction. The sodium is added in pieces of somewhat less than a gram at a time, and in working with quantities not over ten grams the action can be carried on in an open flask without cooling. As soon as all the sodium has disappeared, which takes less than three-quarters of an hour with ten grams of camphor, part of the alcohol is distilled off, and water added, which precipitates crude borneol. This is freed from sodic hydrate by washing with water; after which one crystallisation from the smallest possible amount of hot alcohol is sufficient to raise its melting point to 197°, that of borneol. In this way 10 grams of camphor yielded 9.5 grams of the crude borneol, instead of 10.1 grams; that is, 94 per cent. of the theory; whereas, according to Baubigny's method, 4 grams of sodium, the amount which yielded 9.5 grams of borneol in our process, would have given only 6.6 grams.

Our method, therefore, is superior to the other two in economy, as well as in the ease and speed with which it can be conducted.

¹ Probably a smaller excess of sodium would be sufficient.

MINERALS FROM LEHIGH COUNTY, PA.

BY EDGAR F. SMITH.

1. *Allophane*.

About seven miles from Allentown, near the village of Balliettsville, are numerous iron mines, in which from time to time have been found white, mamillary and stalactitic incrustations upon the ore. In one of these mines a pocket was recently discovered, the inner side of which was completely covered with this coating. The latter has a mother-of-pearl-like appearance, and may be readily detached from the ore by means of a knife. Upon subjecting a portion of this material to a qualitative examination, the presence of water, alumina and silica was revealed. By strong hydrochloric acid, complete decomposition ensued. A quantitative examination yielded the following results:

H ₂ O		40.86 per cent.
SiO ₂		21.39
Al ₂ O ₃		35.20
CaCO ₃ and MgCO ₃		1.96
		99.41

Prof. Prime, in his report on the Geology of Lehigh Co., mentions the occurrence of this mineral in some of the iron mines, but gives no analytical data.

2. *Fluorite*.

About one and a half miles southeast of the above locality are the limestone quarries of Mr. Kleckner. In them have been discovered veins of beautiful fluorite and fine quartz crystals. The former mineral occurs intimately mixed with the limestone, and presents itself in the most beautiful green, purple and pink colors. Upon several specimens octahedral forms were observed, but not very distinct. It is seldom that entire crystals can be procured, since blasting is invariably necessary to reach them; consequently fragments are the result. Quantitative analyses of the purple and green varieties were made.

Purple variety: Fl		49.20 per cent.
Ca		50.87
Fe ₂ O ₃		trace
		100.07

The mean of the specific gravities of five specimens was 3.21; ranging from 3.17-3.24. The shade of purple varied very much in the specimens examined.

Green variety: Fl . . .	49.00 per cent.
Ca . . .	50.91
Fe ₂ O ₃ . . .	trace
	99.91

Sp. gr. about the same as in case of the purple. South of Emmaus in the Lehigh mountains Mr. Benj. Sadtler, Jr., found this mineral in perfect octahedra of deep purple color in a granitic rock.

3. Zircon.

On the farm of Jacob Stine, Esq., Upper Milford Twp., about two miles south of Macungie, are found large quartz fragments distributed over the ground surface. When these are broken, minute crystals are observed here and there in them. Close examination showed these to be perfect forms of zircon—the prism with pyramid being quite distinct; the color of these microscopic crystals varied from a cinnamon to very dark brown. In some of the quartz fragments minute leaflets of graphite and pyrite crystals were seen accompanying the zircon. Enough qualitative tests were made to identify the latter as such. Almost every piece of quartz examined contained one or more crystals of it. Their removal from the matrix was tedious and difficult. Scarcity of material prevented a quantitative examination.

4. Wavellite, etc.

Not more than a quarter of a mile from the above locality and upon the same farm, were found the beautiful crystals of wavellite described by Dr. N. W. Thomas and the writer, Proceedings of American Philosophical Society, March 17, 1882. The first specimens of this mineral were noticed as occurring on limonite; since the publication of the preliminary notice we have obtained, through the liberality of Mr. Stine, a number of specimens lying upon or disseminated through a jasper-like rock which overlies the iron bed. The adjacent land is covered with rock of this character. Mixed with the iron is much pyrolusite. At present

the shaft, in which the most beautiful wavellite was found, is filled with debris. From the quantity of the mineral found at first, and the many points at which it was observed prior to the caving-in of the surface, we may reasonably expect to yet obtain handsome specimens. It usually occurs in beautiful, colorless, radiating nodules on the limonite or jasper-rock.

<i>Analysis.</i>					
Al ₂ O ₃	.	.	.	.	36.66 per cent.
P ₂ O ₅	.	.	.	.	34.14
H ₂ O	.	.	.	.	28.32
Fl	.	.	.	.	trace
Limonite	.	.	.	.	.60
					99.72

Accompanying the wavellite and frequently upon the same specimen were observed nodular, light clay-like forms; sometimes, too, very dark nodules. Some of these revealed no definite radiating structure, while in others this was quite prominent; yet all trace of the white needles of wavellite had completely disappeared. In several instances these nodules were larger than a pigeon's egg. To learn their composition, specimens of both light and dark varieties were analysed. Light variety: sp. gr. 2.5.

H ₂ O	.	.	.	.	.	19.37 per cent.
SiO ₂	.	.	.	.	.	32.42
Al ₂ O ₃	.	.	.	.	.	23.19
Fe ₂ O ₃	.	.	.	.	.	3.82
P ₂ O ₅	.	.	.	.	.	19.19
CaO	.	.	.	.	.	1.00
MgO	.	.	.	.	.	.47
						99.46

Dark variety, sp. gr. 2.40. Analysis:

H ₂ O	.	.	.	.	.	26.29 per cent.
SiO ₂	.	.	.	.	.	6.52
Al ₂ O ₃	.	.	.	.	.	29.37
Fe ₂ O ₃	.	.	.	.	.	15.61
P ₂ O ₅	.	.	.	.	.	22.52
						100.31

5. *Corundum.*

This mineral, which we announced (Am. Phil. Soc. March 17, 1882) as occurring near Shimersville, Upper Milford Twp., has since been discovered there in exceedingly fine crystals; color grayish and red. In many the star is very distinct. The specimens are but slightly altered. The brilliant black crystals noticed upon almost all specimens from here have been found to be menaccanite. Dr. Genth (Am. Phil. Soc. Proceedings, Aug. 18, 1882) has published an account of the black spinel found here, which is unquestionably an alteration of the corundum. Very recently several students of this laboratory discovered fine specimens of it. An analysis of the Shimersville corundum gave the following:

SiO ₂	.	.	.	.	.	.	3.28 per cent.
H ₂ O	.	.	.	.	.	.	1.37
Al ₂ O ₃	.	.	.	.	.	.	85.75
Fe ₂ O ₃	.	.	.	.	.	.	4.26
TiO ₂	.	.	.	.	.	.	2.74
MgO	.	.	.	.	.	.	trace
CaO	.	.	.	.	.	.	1.99

Sp. gravity, 3.898.

99.39

6. *Tourmaline.*

Mr. Benj. Sadtler, Jr., of this laboratory, while searching for corundum at Shimersville, picked up a piece of feldspathic rock, often found here, in which were imbedded three or four large and quite perfect, black crystals of tourmaline. Want of time prevents giving an analysis of the same.

Dr. Henry K. Hartzell, of Allentown, also presented us with a hornblende rock in which were beautiful brown tourmaline crystals, found near what is known as the Bethlehem Iron Co.'s mine on the Lehigh Mt., and not more than 1½ miles northwest of Shimersville. A qualitative examination for identification is all that was made.

On the mountain, two miles south of Allentown, occurs a vein consisting of a brownish-black mineral, which in appearance reminds one greatly of allanite, but the incomplete analysis given below would indicate otherwise, and probably mark it as another occurrence of tourmaline. Its surface in many places is covered

by a reddish colored mineral as yet unexamined. The dip of the vein is about 66°. The analysis as far as made is:

Loss upon ignition,	2.19 per cent.
SiO ₂	39.41
Al ₂ O ₃	19.46
Fe ₂ O ₃ *	8.44
FeO	7.00
CaO	3.49
MgO	2.14
B ₂ O ₃	9.00
Alkalies,	undetermined

7. Garnet.

* At Mohr's magnetite mine in Upper Milford Twp., one-quarter mile from Shimersville, were found rather fine dark-red colored, imperfect dodecahedral crystals of this mineral. They occur in quartz and a granular limestone. The sp. gr. of well-selected material was 4.03, and an analysis of the same gave:

SiO ₂	35.92 per cent.
Al ₂ O ₃	19.18
Fe ₂ O ₃	4.92
FeO	29.47
MnO	4.80
CaO	2.38
MgO	3.70

100.37

Directly south of the above locality upon the land of Mr. Yeakel, quite a large bed of garnet in very minute dark-red crystals has been discovered. It occurs with magnetite.

Near Hosensack Station in Lower Milford Twp., on the Perkiomen R. R., exists a second variety of garnet, found by Mr. E. F. Krauss, '84, in perfect dodecahedral forms of olive color—occasionally the red variety is observed—in a matrix of feldspathic rock. Specular iron ore often accompanies the garnet. The rocks in this region, lying in the most chaotic condition, appear filled with garnets, mostly in well-defined moderately translucent forms. An analysis of the yellow variety gave:

SiO ₂	.	.	.	.	.	35.25 per cent.
Fe ₂ O ₃	.	.	.	.	.	32.17
FeO	.	.	.	.	.	.92
CaO	.	.	.	.	.	30.80
MgO	.	.	.	.	.	trace
						99.14

The specific gravity determined in two specimens was 5.05-5.27.

8. *Stilbite*.

This mineral was first found in Lehigh county, by Mr. E. F. Krauss, upon a limestone in the orchard of Mr. Jacob Schell, near Hosensack station. The specimens are in the form of large globular radiating concretions. Sp. gravity, 2.21.

<i>Analysis.</i>						
SiO ₂	.	.	.	.	.	55.31 per cent.
Al ₂ O ₃	.	.	.	.	.	14.88
Na ₂ O	.	.	.	.	.	1.66
H ₂ O	.	.	.	.	.	18.47
						99.32

9. *Pyrolusite*.

At various times miners have reported this mineral as occurring in Lehigh county, but only of late have finely crystallised specimens of it been observed. The crystals are usually seen upon the inside of limonite nodules, frequently covering their entire inner surface. Those in our possession are from the Lehigh mountain south of Allentown, near the village of Mountainville:

SiO ₂	.	.	.	.	.	9.93 per cent.
Fe ₂ O ₃	.	.	.	.	.	4.21
Al ₂ O ₃	.	.	.	.	.	trace
MnO ₂	.	.	.	.	.	82.66
Mn ₃ O ₄	.	.	.	.	.	3.13
						99.93

10. *Chloropal*.

A little west of the preceding locality are rather extensive iron mines. Over the entire mountain-top holes are observed (dug, evidently, in search of ore), and about these in the debris several

students of this laboratory detected pieces of a yellowish-green colored mineral, so soft as to be readily impressed by the finger-nail. Before the blow-pipe the material, although infusible, gradually assumed a black color and became magnetic; gave strong iron reaction and the silica skeleton. In a closed tube it yielded much water. Since the finding of the above specimens frequent visits have been made to this locality. On a recent trip, while examining some of the larger and deeper excavations, large pieces of the above mineral were noticed about six feet below the surface and overlying the iron deposit. The mineral varies somewhat in color from an olive to greenish-yellow. A number of analyses of the material brought in from time to time by various parties have been made, the results agreeing quite well and pointing to the mineral chloropal. The sp. gr. was found to be 2.033.

Analyses.

	1. Yellow.	2. Dark Yellow.	3. Greenish Yellow.
H ₂ O.	19.61	19.79	18.65
SiO ₂ .	40.20	40.81	42.31
Fe ₂ O ₃ .	39.52	39.30	38.18
FeO.	.40	...	trace
P ₂ O ₅ .	trace	...	...
MgO.	"	...	...
K ₂ O.	"	...	...
	99.53	99.90	99.14
	4. Yellowish Green.	5. Yellowish Green.	6. Light Yellow.
H ₂ O.	20.79	20.45	19.09
SiO ₂ .	41.16	41.41	42.79
Fe ₂ O ₃ .	30.79	35.35	39.19
FeO.	.21	...	...
Al ₂ O ₃ .	2.05	3.04	...
K ₂ O ¹ .	4.54	...	...
	99.54	100.25	101.05
	7. Brownish Yellow.	8. Same as 7.	9. As 7 and 8.
H ₂ O.	19.27	19.31	19.31
SiO ₂ .	42.37	41.35	41.13
Fe ₂ O ₃ .	38.17	39.09	38.97
FeO.	trace	...	...
P ₂ O ₅ .	"	...	trace
MgO.	"	...	"
	99.83	99.75	99.41

¹ This is the only instance where so much alkali was observed.

10. Brown Variety.				11. Yellowish Brown.			
H ₂ O	.	.	17.71		.	.	19.36
SiO ₂	.	.	43.54		.	.	43.00
Fe ₂ O ₃	.	.	39.52		.	.	37.50
100.77				99.86			

The mineral decomposes completely with hydrochloric acid. In all cases the specimens under examination were carefully freed of any adhering ferric oxide, and tested for ferrous oxide, phosphoric acid, calcium and magnesium oxides, and the alkalis. No trace of crystallisation is present. The mineral is earthy in appearance, smooth to the touch, and may be polished by friction.

Some specimens, almost white in color, have been found; one of these gave the following quantitative results:

H ₂ O	.	.	.	.	.	.	17.65 per cent.
SiO ₂	.	.	.	.	.	.	44.52
Fe ₂ O ₃	.	.	.	.	.	.	11.04
Al ₂ O ₃	.	.	.	.	.	.	25.95
MgO	.	.	.	.	.	.	trace
K ₂ O	.	.	.	.	.	.	.94
100.10							

We would here return thanks to our friends and students, Messrs. Benj. Sadtler, Jr., S. C. Schmucker and Ira Wise, for the care and willingness with which they have aided in the execution of the above and other chemical analyses.

MUHLBERG COLLEGE, June 28th, 1883.

SOME MINERALS FROM BERKS COUNTY, PA.

BY D. B. BRUNNER AND EDGAR F. SMITH.

I. *Stilbite*.

At Wheatfield mines we found this mineral in radiating, fibrous, pearly-white masses upon a trap rock, together with exceedingly

beautiful yellow-colored crystals of calcite. Specific gravity 2.2.
An analysis gave:

H ₂ O	19.42 per cent.
SiO ₂	57.49
Al ₂ O ₃	13.03
CaO	8.06
MgO	trace
Na ₂ O	1.36
	99.36

We have also observed stilbite upon a Fritz Island rock in company with mesolite, but not in sufficient quantity to permit of an accurate analysis.

2. *Deweylite*.

In whitish and brownish resinous coatings upon aragonite and together with serpentine at Ruth's mine. Specific gravity 2.3. Analyses of two different specimens afforded us the following:

	A.	B.
H ₂ O	19.49 per cent.	19.03 per cent.
SiO ₂	45.65	42.34
Fe ₂ O ₃	0.20	1.39
MgO	34.38	36.77
CaO	trace	trace
	99.69	99.53

3. *Vesuvianite*.

At Fritz Island there has been for some time found a yellow-colored mineral in limestone, which upon examination gave about the composition of garnet, and was pronounced such until last fall, when we were successful in discovering finely crystallised specimens of the same and now know it to be vesuvianite. Our specimens are yellow in color, and exhibit forms consisting of tetragonal prisms with pyramids.

4. *Titanite*.

This mineral we have observed in clove-brown colored crystals in magnetite from a mine close to Huff's Church, Hereford Township. Our examination of the same, owing to scarcity of material, was limited to qualitative tests.

BRUCITE.

BY DR. J. SCHOENFELD AND EDGAR F. SMITH.

We have specimens of this mineral from two new localities in this State. The first place of interest where we have discovered it in fine large masses together with limestone and in distinct crystalline forms upon a dolomitic rock, is Fritz Island, near Reading. An analysis of a specimen from this locality gave:

MgO	66.78 per cent.
Fe ₂ O ₃	.44
H ₂ O	32.52
	99.74

The second point at which it occurs, although not so abundantly as at the preceding place, is in a limestone quarry, about two miles south of Sinking Spring, Spring Township. This quarry was long operated for magnetic ore, but is now exhausted. The brucite exists in thin, colorless laminae in seams intersecting the limestone rock, much of which is rich in magnesia. On specimens of the dolomitic rock from this place we lately noticed fine silky white fibres, which to qualitative tests revealed the presence of much water, carbon dioxide and magnesia, indicating by these and physical appearance the mineral hydromagnesite. An analysis of the brucite resulted as follows:

MgO	66.19 per cent.
CaO	1.68
Fe ₂ O ₃	1.24
H ₂ O	31.05
	100.16

Contributions from the Sheffield Laboratory of Yale College.

XVI.—ON SOME REDUCTIONS WITH ZINC AND AMMONIA. (SECOND PAPER.)

BY W. G. MIXTER.

Paraazoacetanilide.

It was stated in the footnote to the article (this Journal, 5, 1) on reductions with zinc and ammonia, that azoacetanilide had been obtained. In the experiments there described on the reduction of nitracetanilide, the filtrate from the azoxyacetanilide was exposed for some time to the reducing action of zinc and ammonia, to make sure that no nitracetanilide remained in the solution. The results obtained since show that paraphenylenediamine was formed. If the reduction is stopped after the azoxyacetanilide ceases to separate from the solution in which it is formed, the alcoholic filtrate from the azoxy body leaves a residue on evaporation that contains azoacetanilide and considerable phenylenediamine. The diamine may be dissolved out with highly diluted hydrochloric acid; the undissolved portion, after thorough washing with water, is nearly pure azoacetanilide. It may be purified by dissolving in boiling alcohol and separating the hair-like crystals which form on cooling. Analysis *a* was made with substance obtained from evaporating the filtrate from the crystals, and *b* and *c* were of fibrous crystals of two different preparations. The drying was at 100° C.

a. 0.405 gram yielded 0.9655 gram of CO₂ and 0.2135 gram of H₂O. 0.4015 gram yielded 58.6 cc. of N at 2.4° C. and 766 mm. pressure.

b. 0.4144 gram yielded 0.9861 gram of CO₂ and 0.2083 gram of H₂O. 0.4161 gram yielded 63 cc. of N at 3.2° C. and 766 mm. pressure.

c. 0.3372 gram yielded 0.8005 gram of CO₂ and 0.1678 gram of H₂O. 0.3145 gram yielded 48.45 cc. of N at 4° C. and 750 mm. pressure.

Calculated for C₁₈H₁₆N₄O₂.

		<i>a</i>	<i>b</i>	<i>c</i>
C	64.86	65.01	64.89	64.74
H	5.41	5.85	5.59	5.53
N	18.92	18.40	18.96	18.82

$\text{C}_6\text{H}_4\text{NHC}_2\text{H}_5\text{ON}$
 The azoacetanilide II is a para compound since
 $\text{C}_6\text{H}_4\text{NHC}_2\text{H}_5\text{ON}$

it is derived from paranitracetanilide and converted into para-phenylenediamine by dissolving in strong hydrochloric acid, then adding tin. The azoacetanilide is evidently formed by the removal of one atom of oxygen from azoxyacetanilide, which is the first product of the reduction of the nitracetanilide. In one experiment azoxyacetanilide was dissolved in boiling alcohol and zinc and ammonia and platinum chloride were added. The solution was warmed from time to time until on cooling no azoxyacetanilide separated. After standing a day the solution was evaporated, and the residue after treatment with dilute acid was found to be azoacetanilide. Paraazoacetanilide melts at $281-2^\circ\text{C}$., has the color of gold, is insoluble in water, and is more soluble in alcohol than azoxyacetanilide.

Paraazoaniline.

Paraazoacetanilide dissolves in hot concentrated hydrochloric acid, both acetyl groups being replaced by hydrogen, with formation of a hydrochloride, which remains as a black mass after the solution has been evaporated on a water-bath. From the aqueous solution of the hydrochloride the base was precipitated with ammonia and was washed with water and dried at 100°C . Analyses I and II show the composition of this precipitate. The same compound was also formed by the saponification of azoacetanilide, which was obtained by reducing pure azoxyacetanilide as already described. Analyses III and IV show its composition.

I. 0.3158 gram yielded 0.7833 gram of CO_2 and 0.1621 gram of H_2O .

II. 0.2176 gram yielded 46.2 cc. of N at 4°C . and 763 mm. pressure.

III. 0.3555 gram yielded 0.8805 gram of CO_2 and 0.1838 gram of H_2O .

IV. 0.2053 gram yielded 43.2 cc. of N at 4°C . and 760 mm. pressure.

	Calculated for		I.	II.	III.	IV.
	$\text{C}_{13}\text{H}_{14}\text{N}_4$	$\text{C}_{13}\text{H}_{12}\text{N}_4$				
C	67.29	67.93	67.64		67.55	
H	6.54	5.66	5.70		5.74	
N	26.17	26.41		26.39		26.05

The results correspond best with $\text{C}_{13}\text{H}_{12}\text{N}_4$.

Diamidohydrazobenzene, $C_{12}H_{14}N_4$, melts at $145^\circ C$.¹ Chrysoidine, $C_{12}H_{12}N_4$,² melts at $110^\circ C$., and forms the salt $C_{12}H_{12}N_4HCl$.

Hofmann suggests the formula C_6H_5N || for chrysoidine, $C_6H_3(NH_2)_2N$

since it yields with nascent hydrogen aniline, and according to Griess triamidobenzene. The substance analysed melts at $235-240^\circ C$. and appears to form the hydrochloride $C_{12}H_{12}N_4 \cdot 2HCl$. A weighed quantity of the substance was evaporated with hydrochloric acid, and the increase in weight corresponded with that required by the addition of two molecules of hydrochloric acid. Nascent hydrogen converts the new compound into paraphenylenediamine, an evidence that each benzene group contains one NH_2

group as represented by the formula $C_6H_4NH_2N$. || The name $C_6H_4NH_2N$

paraazobenzene which indicates this constitution is proposed. The writer has been unable to find any description of an azobenzene. Haarhaus³ attempted to make diamidoazobenzene, *i. e.* azobenzene by reducing paranitraniline with sodium, but obtained diamidohydrazobenzene. Platinum chloride precipitates in a concentrated aqueous solution of the azobenzene hydrochloride, a salt which is somewhat soluble in water and very soluble in alcohol. Three preparations of the salt, dried at $100^\circ C$., yielded respectively 28.14, 28.53 and 27.80 per cent. of platinum. Theory requires 31.2 per cent. of platinum in $C_{12}H_{12}N_4H_2PtCl_6$ and 23.6 per cent. in $(C_{12}H_{12}N_4)_2H_2PtCl_6$. The quantity of platinum salt obtained was too small for complete analysis. Azobenzene has a dark yellow color, is slightly soluble in water and very soluble in alcohol, and its solutions have considerable coloring power. The solutions of its salts are red.

Paraazoxybenzanilide.

Mr. A. W. Robert, a student in this laboratory, has prepared the paraazoxybenzanilide by the method employed in making the metaazoxybenzanilide.⁴ Pure paranitracetanilide was made and converted into paranitraniline. The nitraniline was heated with benzoyl chloride, and the paranitrobenzanilide formed was thor-

¹ Lermontow, *Berichte der deutschen chemischen Gesellschaft*, **5**, 232.

² Hofmann, *Ibid.* **10**, 214, 390.

³ *Annalen der Chem. u. Pharm.* **135**, 162.

⁴ This Journal, **5**, 5.

oughly washed with hot water and then recrystallised from boiling alcohol. It melted at 199° C. The following is the analysis of the azoxybenzanilide:

I. 0.3607 gram yielded 0.9417 gram of CO_2 and 0.1519 gram of H_2O .

II. 0.316 gram yielded 33.4 cc. of N at 10° C. and 765 mm. pressure.

III. 0.2123 gram yielded 23.1 cc. of N at 14° C. and 762 mm. pressure.

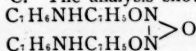
	Calculated for $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_2$.	I.	II.	III.
C	71.56	71.23		
H	4.58	4.67		
N	12.85		12.92	13.04

The paraazoxybenzanilide melts at 310° , has a light yellow color, and is insoluble in alcohol and water. It dissolves readily in strong alcoholic potash, which converts it, on boiling, into paraazoxyaniline.

The alcoholic filtrate from the azoxybenzanilide was evaporated to dryness, and the residue was treated with boiling water and filtered hot. The portion insoluble in water was recrystallised from alcohol and analysed. The results indicated a mixture containing much unreduced nitrobenzanilide. The azobenzanilide looked for was not found. The hot aqueous solution yielded, on cooling, pearly crystals, which gave 13.11 per cent. of nitrogen and a platinum salt with 22.62 per cent. of platinum, results which indicate an impure amidobenzanilide. Theory requires 13.3 per cent. of nitrogen in the pure substance and 23.77 per cent. of platinum in its platinum salt. The substance melted at 110° C. Hübner states the melting point of paraamidobenzanilide at 128° C.¹

Azoxybenztoluide.

Nitrotoluidine, melting point 77.5° C., was treated with benzoyl chloride, and the nitrobenztoluide, after washing with water, was dissolved in boiling alcohol and reduced with zinc and ammonia. The substance which separated from the solution was washed with alcohol, shaken with dilute hydrochloric acid, and finally washed with water, and dried at 100° C. The analysis shows that the compound is azoxybenztoluide



¹ Annalen der Chemie, **208**, 295.

I. 0.427 gram yielded 42 cc. of N at 10° C. and 762.4 mm. pressure.

II. 0.4515 gram yielded 1.189 gram of CO₂ and 0.2166 gram of H₂O.

III. 0.3554 gram yielded 1.0148 gram of CO₂ and 0.1844 gram of H₂O.

	Calculated for C ₂₈ H ₂₄ N ₄ O ₃ .	I.	II.	III.
C	72.41		71.82	71.81
H	5.17		5.33	5.31
N	12.07	11.96		

Azoxybenztoluide melts at 290° C., has a light yellow tint, and is insoluble in water and alcohol.

Attempts to replace the benzoyl group by hydrogen have failed to yield azoxytoluidine, which Buckney has described.¹ Oil of vitriol at 100° and hydrochloric acid at 180° were tried.

The azoacetanilide and azoaniline complete the analogy indicated in the former paper² between the reduction products of nitrobenzene and those of paranitracetanilide, with the exception that no hydrazobenzene or benzidine analogue has as yet been obtained. The metaoxybenzanilide is the only meta compound of the series made thus far in the investigation. Experiments with impure orthonitracetanilide yielded only negative results. Perhaps orthonitrobenzanilide would give an azoxy body because of the greater insolubility of azoxybenzoyl compounds in alcohol. The results thus far obtained indicate that the hydrogen from zinc in ammoniacal solutions does not differ essentially from nascent hydrogen from other sources. The action of zinc and ammonia is less violent than that of zinc and acids, and is apparently better adapted to the formation of azo compounds. Zinc and ammonia do not separate the acetyl and benzoyl groups as would the fixed alkali in case sodium amalgam or caustic potash is used. Modifications of the method employed by the writer may perhaps be advantageously adopted. The presence of considerable ammonium chloride increases the evolution of hydrogen from zinc in solutions containing ammonia, and perhaps sodium amalgam may replace zinc with advantage in solutions containing sufficient ammonium salt so that sodium hydroxide cannot exist in the solution.

¹ Berichte der deutschen chemischen Gesellschaft, 11, 1452.

² This Journal, 5, 7.

A CONVENIENT TEMPERATURE REGULATOR.

BY W. T. RICHMOND.

Notwithstanding that various forms of electrical temperature regulators have from time to time made their appearance, the following form of apparatus, devised and used with success by the writer in the laboratory of the Northern Transcontinental Survey, will, it is hoped, be found useful.

The apparatus may be said to consist essentially of three parts: A glass bulb *A*, a U tube *B* (Fig. I), and an apparatus *C* (Figs. I and II) by means of which the gas is turned off and on.

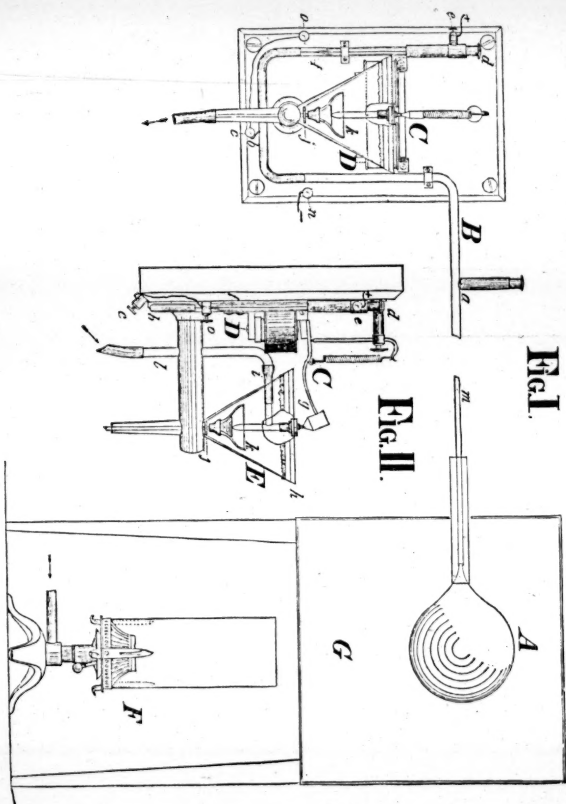
The glass bulb *A* is very conveniently made by drawing out the neck of a flask before the blowpipe, and fusing a glass tube of such a diameter that it will easily fit in the end of the U tube to the outdrawn neck. A larger piece of tubing is then put over the joint and plaster of Paris poured between. When the plaster sets the joint will be much strengthened. The U tube *B* (Fig. I) has a T joint at *a*, to the top of which is cemented a screw top, by means of which the regulator may be set at any temperature by leaving the top unscrewed until the required temperature is reached, at which degree the top is to be screwed down tight on the washer. In the middle of the U tube is a piece of platinum wire *b*, fused in the glass, so that the mercury which the tube contains will always be in contact with it. The wire is connected with a screw-cup *c*, which diminishes the danger of breakage. At the left-hand extremity of the tube is a screw-top *d* and screw-cup *e*. The screw-top *d* is to be tightly screwed down on the washer when the regulator is to be used for any great length of time, as by this means the barometric variations are without effect on the mercurial column. For ordinary use the top may be left unscrewed. A platinum wire *f*, having metallic connection with the screw-cup *e*, passes down the tube to within a short distance of the mercury. The wire is fused in a small piece of tubing, as shown in the figure. By this means the air space of the U tube is diminished, and consequently the liability of the mercurial column being influenced by the outside temperature. The screw-cup *e* is, of course, for the battery wire.

The part of the apparatus *C* (Figs. I and II) consists of an electro-magnet *D* and a funnel *E*. The armature of the electro-

magnet has affixed to it a brass rod *g*, and is connected at its extremity with the rubber diaphragm *h*, which covers the mouth of the funnel, being held in place by a rubber band. A spring is seen connected with the armature, which serves to bring it back to its original position after the electro-magnet ceases to act. The glass funnel *E* is about four inches in diameter. Through the side of the funnel is drilled a small hole of such a size that the piece of rubber tubing *i* fits gas-tight. To the centre of the rubber diaphragm *h* is attached a small T tube, as represented in Fig. II, the T of which is attached to the rubber tubing *i* conveying the gas. Through the neck of the funnel passes a brass rod having a thread cut on it and working in a nut *j*, which rests at the junction of the funnel and neck. The upper part of the rod carries a cup *k*, in which is put a little mercury, or what is perhaps better than the cup, a rubber stopper. It will be obvious that the screw-working rod acts only as an aid in adjusting the apparatus when it is first put up.

One part of the T tube is attached to the rubber diaphragm *h*, while the other, through which the gas passes when not shut down, is just a little above the mercury cup or stopper. The whole T works on the flexible joint *z*. The T tube has a small hole in it through which just enough gas passes to keep the Argand burner *F* lighted when the diaphragm *h* is pressed down. The gas passes into the apparatus through the glass tube *b*, as indicated by the arrow, out through the neck of the funnel, whence rubber tubing takes it to the burner *F*.

The apparatus is set up and worked as follows: The glass bulb *A* (Fig. I) is placed in the air-bath *G*, and the smaller piece of tubing *m* is pushed into the end of the U tube *B*, where it is cemented by means of plumber's cement. The gas is let into the apparatus, the Argand burner is lighted, the screw-top *a* is opened; the nut-working rod is screwed up until the mercurial cup or rubber stopper is near enough to the orifice of the T tube delivering the gas to cause the flame to fall when the diaphragm is slightly depressed. One wire of the battery is connected with the screw-cup *e*, the other being placed in connection with screw-cup *n*. A piece of copper wire connects *o* and *c*, *n* and *o* being the ends of the electro-magnet wire. When the proper temperature is reached, as indicated by the thermometer in the air-bath, the screw-top *a* is screwed down tight. The residual air in *A* con-



tinuing to expand, pushes the mercury in the U tube until it comes in contact with the platinum wire *f*. At this instant the electric circuit is completed, the electro-magnet attracts the armature, the diaphragm *h* is depressed, the flow of gas is almost entirely cut off, the flame of the burner falls, the temperature sinks, the air in the bulb contracts, the mercurial column breaks contact with *f*, the spring attached to the armature draws the diaphragm back to its original position, the free flow of gas again takes place, and the apparatus is again in its former condition, the alternations of course taking place as often as contact is made and broken by the mercurial column and *f*.

I find plumber's cement to be well adapted for cementing the screw tops to the U tube.

The diaphragm covering the mouth of the funnel may be made of rubber or other flexible gas-tight material.

The mercury used in the U tube should be perfectly *clean*.

The apparatus made as above described will, I find, keep the temperature constant to within $\frac{1}{2}^{\circ}$ – 1° , provided the flame of the burner is not so large as to overheat the air-bath before the air-bulb has time to respond.

In conclusion I wish to thank Mr. Whitfield, Assistant Chemist to the Northern Transcontinental Survey, who kindly prepared the drawings from which the above cut was made.

THE VOLUMETRIC DETERMINATION OF MANGANESE.¹

BY J. B. MACKINTOSH.

In a recent paper read before the Institute on this subject, Mr. G. C. Stone advances the theory that the precipitate obtained in Williams's volumetric process,² by treating the boiling nitric acid solution of a manganese salt with potassic chlorate, is not pure

¹ Read at the Roanoke Meeting of the American Institute of Mining Engineers.

² Transactions of the American Institute of Mining Engineers, 10, 100.

MnO_2 , but approximates more closely to the composition $10\text{MnO}_2 + \text{MnO}$.

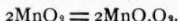
As the value of the process and the accuracy of our results would depend on whether this was the fact or not, it has seemed to me, and to my associates, Messrs. Beebe and Colby, that it would be of importance to ascertain the composition of this precipitate, and to that end the following series of experiments has been undertaken.

These experiments have all been based on the considerations:

1. That potassic permanganate has an oxidising power equivalent to five atoms of oxygen for every two of manganese:



2. That the same amount of manganese in the state of binoxide, has an oxidising power equivalent to two atoms of oxygen:



If, then, we take a solution of permanganate of unknown strength, and reduce it to binoxide, the oxidising power of the binoxide formed will be equal to that of two-fifths the quantity of the permanganate solution originally taken. While, if the precipitate obtained should not be binoxide, but an indefinite or definite mixture of bin- and mon- oxides, then, from its equivalent oxidising power, we can calculate its composition.

The analyses were conducted in the following manner. The amount of permanganate taken was decomposed with hydrochloric acid, and concentrated to expel the excess of water. Sufficient excess of nitric acid was now added, and the solution was boiled until all the hydrochloric acid was destroyed. The manganese was then precipitated by potassic chlorate; and, after standing some time to cool—a precaution which we consider of importance—the precipitate was filtered out through asbestos, washed with nitric acid, and then with water, and when perfectly clean was treated with a volume of oxalic acid, whose equivalent in permanganate was known, a few cubic centimeters of sulphuric acid being also added. The excess of oxalic acid was then estimated by permanganate, and the difference between this amount and the equivalent of the whole amount of oxalic taken gave the oxidising power of the precipitate.

To save multiplication of figures we will only give the results obtained:

$K_2Mn_2O_8$ used.	Oxidising power of precipitate in terms of $K_2Mn_2O_8$.	Theoreti- cal for MnO_2 .	Apparent per cent. of theoretical.	Corrected per cent. for burette error.
cc.	cc.	cc.		
45	17.80	18	98.89	99.37
35	13.93	14	99.50	100.07
25	9.90	10	99.00	99.86
15	5.96	6	99.33	100.67

Average true per cent., 99.99

The precipitation in the above results was affected by successive alternate additions of potassic chlorate and nitric acid, until no further formation of yellow fumes was observed. Shortly after first employing the method, we noticed that the reaction was seldom complete when potassic chlorate was added during one period only, and that if, after the apparent completion of the reaction, as marked by the explosive cessation of yellow fumes, more nitric acid was added, and then a fresh portion of potassic chlorate, the yellow fumes would reappear, again to disappear with the characteristic puff. On this account it is necessary in employing this method, to add alternate amounts of nitric acid and potassic chlorate, until no further effect is produced; and, if this precaution is not observed, the results will almost invariably be low.

The next series of experiments was made to illustrate this point, and to determine the amount of error which would be incurred by exactly following the directions given by Messrs. Ford¹ and Williams in their respective papers, namely, by adding potassic chlorate during one period only and boiling till the apparent cessation of the reaction. The results obtained were as follows:

$K_2Mn_2O_8$ used.	Oxidising power of precipitate in terms of $K_2Mn_2O_8$.	Theoreti- cal for MnO_2 .	Apparent per cent. of theoretical.	Corrected per cent. for burette error.
cc.	cc.	cc.		
40	15.55	16	97.20	97.82
45	17.70	18	98.33	98.92
60	23.37	24	97.40	98.04

Showing an error of from one to two per cent.

The following determinations were made about last February, but no particular record of the details of the manipulation were preserved:

25	9.93	10	99.30	98.34
50	19.73	20	98.65	99.07

¹ Transactions of the American Institute of Mining Engineers, 9, 397.

It is evident from inspection of these results, that the first set approach very nearly to the theoretical figure for MnO_2 , the average of the four happening to be 99.99 per cent. This close agreement with theory must, however, be considered as largely accidental, as the variation in the separate determinations is quite large. In a process of this kind we must consider that the experimental errors are relatively large; indeed, larger than in the actual application of the method to analysis. These experimental errors, doubtless, balance each other to a large extent by averaging several results, as in the present instance; but we can hardly expect to get such close average results every time.

The burette was calibrated for each analysis by weighing the amount of water delivered corresponding to the various volumes used, and making proportional corrections.

Now, if the composition of the precipitate had been $10\text{MnO}_2 + \text{MnO}$, as claimed by Mr. Stone, the oxidising power found should have averaged 90.91 per cent. of the theoretical figure for MnO_2 , instead of that which we have actually found; so that the difference is far too great to admit of any doubt as to the true composition of the precipitate. We may safely conclude, then, that the precipitate obtained in this process, when due regard is paid to the precautions which we have indicated, is MnO_2 , and not an indefinite or definite mixture of oxides, that the process is reasonably accurate, and that any estimation based upon the theory that the precipitate is not MnO_2 is of no value, because it is founded on false premises, and therefore can never be true save by accident.

REVIEWS AND REPORTS.

THOMSEN'S "THERMOCHEMICAL RESEARCHES."¹

Three years ago Berthelot's important treatise on thermochemistry appeared, and now the literature of the subject is still further enriched and the work of students facilitated by the publication

¹ Thermochemischen Untersuchungen. Von Julius Thomsen. Leipzig, Barth, 1882.

in book form of Thomsen's numerous and valuable researches, which in main part have appeared in various scientific journals from time to time during a long series of years. The author announces that the work is to consist of four volumes, entitled as follows: I. Neutralisation; II. Metalloids; III. The Metals; IV. Organic Compounds. The greater part of the material of the first three volumes has already been published in separate papers. Considerable additions of new material and revisions and redeterminations in the old have, however, been made.

The fourth volume will be essentially new, only one or two brief publications having been made of the author's researches in the thermal phenomena of organic compounds. And the nature of these communications leads one to anticipate that volume IV will be of the greatest interest. At the time of writing only volumes I and II are in print.

One cannot but be impressed by even the first half of the work with the enormous amount of patient and skilled labor involved in these extended researches, and the whole may justly be termed colossal. In his first volume Thomsen gives but a brief exposition of the general principles upon which the science of thermochemistry is based. Indeed, judging from the two volumes at present in print, we should say that for the systematic development of the science of thermochemistry, or, more broadly speaking, of chemical mechanics based upon thermochemistry, of its general principles and of its relations to other branches of physics, Berthelot's treatise is superior. For the precise and accurate determination of the fundamental numerical data, which must, of course, furnish the basis of the system, the comparison might perhaps be more in favor of Thomsen's work. Fortunate it certainly is for the science that the parallel labors of these two eminent investigators furnish results which control and, in general, confirm each other.

Volume I contains the results of about 1100 calorimetric determinations, involving some 600 chemical reactions. The greater part of these pertain to the thermal phenomena of neutralisation proper, involving the detailed study of the combination of some 45 different acids, organic and inorganic, with sodic hydrate; and on the other hand of 42 bases, organic and inorganic, with sulphuric, hydrochloric, nitric and some other acids. In these experiments acid and base are present not only in equivalent quantities, but the effect of acid and base in excess upon the phenomena is studied, and conclusions drawn therefrom with reference to basicity of acid and to the existence of acid and basic salts in solution. In this way the calorimeter in many cases confirms the accepted notions upon the subject, and in some solves questions which purely chemical methods fail to answer. In addition to these elementary data the author treats, more or less briefly, some points of more immediate and general interest, viz. the thermal phenomena of single, double and partial decomposition, and the so-called "avidity" of acids, which is determined in 17 cases; the

role of water in aqueous solution, the specific heat of solutions, and the variations of heat disturbance with temperature.

A valuable feature of the work is that the actual experimental data used in the calculation of final results are given in detail. For example, take a single determination of the heat evolved in neutralising sulphuric acid with sodic hydrate, or as Thomsen expresses it, $\text{Na}_2\text{OAq}, \text{SO}_3\text{Aq}$. We find given:

Temperature of air	$= T = 18.3^\circ$
" " NaHO Sol.	$= t_a = 18.545^\circ$
" " H_2SO_4 "	$= t_b = 18.468^\circ$
" on mixing	$= t_c = 22.801^\circ$
Heat disturbance in calorimeter	$= r = 3921$
Fraction of molecular wt. used	$= s = \frac{1}{2}$
Heat disturbance for molecular reaction	$= R = 31368 \text{ cal.}$

The general formula used by Thomsen to calculate the value of r is

$$r = (t_c - t_a)a + (t_c - t_b)(b + p) + q_{450}^a, \quad (1)$$

in which a is the weight of water in first solution, b of second, p the calorific equivalent in H_2O of calorimeter and its appurtenances, and q a constant correction for difference in the reading of thermometers used; the other letters having the significance indicated above. In the experiment cited $a = b = 450$ grams, $p = 13$ grams, $q = 0$. In general the solutions of acid and base contain 200 H_2O for one equivalent of substance.

It will be seen that the above formula (1) is based upon the assumption that the calorific equivalent of the resulting salt solution is equal to the sum of the calorific equivalents of its constituent acid and base solutions, and that the calorific equivalent of each of the latter is equal to the weight of water therein contained.

As this assumption is only approximately true, the formula based upon it gives only approximate results. The exact formula, omitting the correction for thermometer readings, would be the following:

$$r = (t_c - t_m)(m + p) \quad (2)$$

in which t_c = observed temperature after mixing.

t_m = " " of constituent solutions before mixing, supposing them to be at the same temperature.

m = calorific equiv. of resulting salt solution.

p = " " of calorimeter and belongings.

If the constituent solutions are not at the same temperature before mixing, t_m would be given by the formula,

$$t_m = \frac{a t_a + (b + p) t_b}{a + (b + p)}$$

in which a and b are calorific equiv. of base and acid solutions, and t_a and t_b their respective temperatures. This may be simpli-

fied to $t_m = \frac{t_a + t_b}{2}$ without introducing appreciable error in the usual conditions of experimentation. The error introduced by the assumption which Thomsen uses for the calculation of the amount of heat disturbance is probably small also, when the solutions have the degree of dilution generally employed, viz. 200 H₂O for one equiv. of substance. How small the error is only a special determination of the specific heat of the given solutions can show. For example: the reaction $\text{Na}_2\text{O} + 200\text{H}_2\text{O} + \text{H}_2\text{Cl}_2 + 200\text{H}_2\text{O} = \text{Na}_2\text{Cl}_2 + 401\text{H}_2\text{O}$ gives by formula (1) the value 3438 for r . Calculated by formula (2), using Thomsen's determination of the specific heat of $\text{Na}_2\text{Cl}_2 + 400\text{H}_2\text{O}$, $r = 3408$, a difference of .87 per cent. In most cases the error is probably less than this, but it is evident that it may be safely neglected only when the solutions are considerably diluted and the change in temperature small. In these conditions the actual specific heat being unknown, Berthelot assumes for the purpose of approximate calculation that the calorific equivalent of 1 cc. of the primitive solution is equal to that of 1 gram of H₂O. Thus the volume of $\text{HCl} + 100\text{H}_2\text{O} = 1818.5$ cc. (temperature 18°), of $\text{NaHO} + 100\text{H}_2\text{O} = 1795.9$ cc.; their sum 3614.4 is the cal. equiv., by Berthelot's assumption, of $\text{NaCl} + 201\text{H}_2\text{O}$. By Thomsen's hypothesis this quantity is 3600. On the assumption that the specific heat of the solutions is 1 (which is often made) this value is 3676.5. The experimental determination of it by Thomsen gives 3596.

The author gives a short chapter to the subject of the variation of heat disturbance with temperature. With a knowledge of the specific heat of the solutions in question, the amount of this variation for one degree of temperature may be calculated by the formula

$$\phi = \frac{R_T - R_t}{T - t} = q_a + q_b + q_c, \text{ in which } R_T \text{ and } R_t \text{ represent}$$

the heat disturbance for the temperatures T and t ; q_a and q_b represent the quantities of heat required to raise the component solutions from t to T , and q_c the quantity required to raise the resultant solution from t to T . This formula is derived directly from the second principle of thermochemistry, called by Berthelot the principle of "Initial and Final State."

Thomsen gives a few instances of the experimental determination of this variation of heat disturbance between the temperatures of 9 and 25°, and compares these values with those calculated by the above formula and the specific heats determined by himself. The reactions are those involved in the formation of Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, NaCl and NH_4Cl in the usual conditions. The results are respectively:

ϕ by direct experiment.

— 27 cal.
+ 69
— 43
+ 2.6

ϕ by formula.

— 29 cal.
+ 65
— 45
— 3

In spite of the considerable accordance between these series of differences, we doubt very much whether the quantities are far enough removed from the limits of experimental error to be much relied upon.

One of the most interesting points considered in Thomsen's first volume is the so-called avidity of acids or partial decomposition in aqueous solution. When two given acids in equivalent quantities are brought in contact with one equivalent of base in aqueous solution, there is in certain cases a division of the base between the acids. The ratio of the fractions of the base thus divided is, according to Thomsen's definition, the relative avidity of the acids.

For example, when 1 equiv. of sulphuric acid and 1 equiv. of nitric acid are in presence of 1 equiv. of sodic hydrate, it is found that $\frac{1}{3}$ of the base is in combination with the first and $\frac{2}{3}$ with the second acid. Making the avidity of hydrochloric acid unity, that of sulphuric acid .50. To determine the quantity of base combined with each acid is a difficult problem, since all the substances remain in solution. Thomsen succeeds in solving it by calorimetric methods. Without giving the details of the process we may state that to determine the avidity of H_2SO_4 and HNO_3 , the heat disturbance of the following reactions must be measured:

1. Neutralisation of H_2SO_4 by NaHO .
2. " " HNO_3 " "
3. Decomposition of Na_2SO_4 by HNO_3 .
4. " " NaNO_3 by H_2SO_4 .
5. Sulphate + H_2SO_4 in varying quantity.
6. Nitrate + HNO_3 " "
7. H_2SO_4 + HNO_3 .

The author finds that the relative avidity varies with the base employed, but is apparently independent of the degree of dilution and of the temperature, or at least the variation is so small as to escape measurement by his methods. He finds no relation apparent between relative avidity and heat of neutralisation or the basicity of the acid. Nor do his results accord with Berthollet's theory of partial decomposition. They do, however, afford a satisfactory experimental test of the correctness of the theory of Guldberg and Waage. Berthollet's theory for the division of a base between two acids is formulated by Thomsen as follows: let b and b' represent the fractions of the base in combination with the acids; M and M' their respective masses, and x and x' their "affinities." Then $\frac{b}{b'} = \frac{Mx}{M'x'}$; but $M = \frac{aA}{g}$ and $M' = \frac{a'A'}{g}$ in which A and A' are the equivalents of the acids, and a and a' the number of equivalents present; hence $\frac{b}{b'} = \frac{aAx}{a'A'x'}$. "Affinity" is defined by Berthollet as the reciprocal of equivalent; hence $\frac{x}{x'} = \frac{A'}{A}$ and the formula becomes $\frac{b}{b'} = \frac{a}{a'}$. Further, if there are B equiva-

lents of base present, $b + b' = B$. From these two equations $b = \frac{aB}{a + a'}$ and $b' = \frac{a'B}{a + a'}$. This formula is evidently not in accordance with fact, since b and b' have by it the same value for any couple of acids. If we make $a = a' = B = 1$, then $b = b' = \frac{1}{2}$, which is certainly not true for many couples.

If instead of $\frac{b}{b'} = \frac{a}{a'}$ we use $\frac{b}{b'} = \frac{m}{m'} \cdot \frac{a}{a'}$, in which $\frac{m}{m'}$ is constant for the same system of base and acids, it will be seen that when $a = a'$, $\frac{b}{b'} = \frac{m}{m'}$, or in other words that $\frac{m}{m'}$ is the ratio of Thomsen's so-called avidities. From this modified formula we obtain $b = \frac{amB}{am + a'm'}$ and $b' = \frac{a'm'B}{am + a'm'}$. The values of b and b' given by these formulas are compared with the values given by experiment when the system is made up of Na, H_2SO_4 , and HNO_3 . Here $\frac{m}{m'} = \frac{1}{2}$ as determined calorimetrically by Thomsen, or in other words, the avidity of HNO_3 is twice that of H_2SO_4 . In the conditions of the experiment $a = B = 1$ and a' is variable. The following table gives the results:

a'	Exp.	Theo.
$\frac{1}{2}$	— 904 cal.	— 1456
$\frac{1}{3}$	— 1616	— 2626
$\frac{1}{4}$	— 2584	— 3010
1	— 3504	— 3548
2	— 4052	— 3824
3	— 4100	— 3918

The third column gives the heat disturbance calculated for the values of b and b' given by the above formula, while the second column gives the values obtained by experiment. It will be seen that the theory does not accord with fact. If we turn to the theory of Guldberg and Waage, we find better success. This theory as applicable to the cases experimented upon may be formulated as follows: Let P and Q represent two substances which by double decomposition produce R and S ; a, b, c, d , the number of equiv. of each present before reaction; x the number of equivalents decomposed. Then after the reaction the system becomes $(a - x)P + (b - x)Q + (c + x)R + (d + x)S$. Let K represent the force by which $P + Q$ tend to become R and S , and $1/K'$ the force of the opposite reaction, $R + S = P + Q$. Now by this theory $K(a - x)(b - x) = 1/K'(c + x)(d + x)$. Putting for convenience $KK' = n^2$ and finding the value of x gives

$$x = \frac{n^2(a+b) + c + d - \sqrt{[n^2(a+b) + c + d]^2 - 4(n^2 - 1)(n^2 ab - cd)}}{2(n^2 - 1)}$$

To apply this formula the value of n must be determined. This is done by measuring x experimentally with given values for a , b , c , and d . In the case under consideration, viz. the reaction $\text{Na}_2\text{SO}_4 + 2\text{HNO}_3$, when $a=b=1$ and $c=d=0$, $x=\frac{2}{3}$ determined calorimetrically by Thomsen. Substituting in formula gives

$$x = \frac{n}{n+1} = \frac{2}{3}, \text{ whence } n = 2.$$

Substituting this value of n in the formula gives

$$x = \frac{4(a+b) + c + d - \sqrt{[4(a+b) + c + d]^2 - 12(4ab - cd)}}{6}$$

From this x may be calculated for all values of a , b , c and d . In the following table are compared the values given by this theory and those given by experiment; the system being Na , H_2SO_4 , HNO_3 :

$a = 1$			
$b = c = 0$			
b	x	Exp.	Theo.
$\frac{1}{8}$	0.121	904 cal.	924 cal.
$\frac{1}{4}$	0.232	1616	1656
$\frac{1}{2}$	0.423	2584	2662
1	0.667	3504	3546
2	0.845	4052	3948
3	0.903	4100	4038

Similarly the results of four other series of experiments are compared by the author with the results deduced from the theory, and in no case is the difference more than .3 per cent. of the heat of neutralisation. The agreement becomes more remarkable when we consider that the calculated experimental values involve the determination of at least three different quantities.

If in the equation $K(a-x)(b-x) = 1/K'(c+x)(d+x)$, we make $a=b=1$ and $c=d=0$ and $KK' = n^2$, then by reducing $n = x/1-x$. But x and $1-x$ are the fractions of the base in combination with the two acids respectively when 1 equiv. of each substance is present. Hence n becomes the relative avidity of the two acids for the given base, according to Thomsen's definition.

Another point in Vol. I. may be mentioned as of general interest, viz. the author's conclusion that, for the same acid, the true heats of neutralisation in solution are the same for the alkalies, the alkaline earths and the magnesium bases, Mg, Mn, Ni, Co, Fe, Cd, Zn and Cu; and that where there is an apparent difference, it is due to difference in the heat of solution; and, further, that in solution, as in the gaseous form, we have a condition which permits the comparison of the physical properties of substances in their simplest relations.

A. V. E. YOUNG.

NOTES.

Contributions to the Chemistry of the Cerite Metals.

The figures hitherto obtained in the determinations of the atomic weight of didymium vary between the limits 142 and 147.2. The most recent determinations are those of Cleve (147.2) and Brauner (146.58)¹. As the difference of more than five units between the above numbers is greater than could be attributed to mere experimental errors, B. BRAUNER "undertook experiments to decide which of the numbers represents, or more nearly approaches, the true atomic weight of didymium, and to ascertain whether pure didymium is a homogeneous body, or whether it can be split up into heterogeneous constituents, as has proved to be the case with several metals of the rare earth group." Didymium oxide was, for this purpose, purified in three ways and the atomic weight determined. It was found to be 145.42, the determinations differing only between the limits 145.53 and 145.31. This number differs very sensibly from those found by Cleve, viz. $Di = 147.2$, and from those obtained in the author's former experiments, viz. $Di = 146.58$, and this difference cannot be attributed to mere experimental errors. On the contrary, the true reason of this discrepancy may, as it seems, be looked for in the circumstance that an element of a higher atomic weight and of a less basic nature than didymium was eliminated from the original oxide, by precipitating the small traces of cerium present, together with a portion of the didymium with ammonia.

A careful examination showed that the element of a higher atomic weight is samarium. The highest atomic weight obtained was 149.4. The substance giving this result was found to contain 25.2 per cent. of didymium, so that the atomic weight of samarium deduced from these data is $Sm = 150.7$. The atomic weight of the purest didymium prepared is $Di = 145.4$, which number may be assumed to represent, as nearly as possible, the true atomic weight of didymium.—(*Journal of the (London) Chemical Society*, 1883, 278.)

A new Substance in Benzene from Coal Tar.

In a recent number of this Journal² attention was called to some observations made by VICTOR MEYER, which led to the conclusion that there is some difference between the benzene obtained from coal tar and that from benzoic acid. The author has continued his experiments, and has succeeded in isolating from coal tar benzene a peculiar substance containing sulphur, which he calls

¹ When O = 16 and S = 32.07.² Vol. 3, 481.

thiophene. It is this substance which gives to benzene the power to unite with isatin, phenylglyoxylic acid, benzoyl cyanide, etc., in the presence of sulphuric acid. The fact that coal tar benzene is turned brown by concentrated sulphuric acid, while pure benzene is not affected in this way, is also due to the presence of thiophene in the former.

The isolation of thiophene was effected in a chemical factory. 250 litres of the purest commercial benzene were shaken for four hours with 25 litres of concentrated sulphuric acid. After the removal of the layer of benzene, the black acid mass was diluted with water and the lead salt of the sulphonic acid prepared. The quantity of salt obtained in this way—mainly the lead salt of the new sulphonic acid together with some benzenesulphonate—amounted to 16 kilograms. From the lead salt the new body may be obtained easily in large quantity. It is decomposed by means of hydrogen sulphide and then subjected to dry distillation, or it is distilled with hydrochloric acid, or with ammonium chloride. In either way there is obtained a light volatile oil which boils for the greater part at 84° . This product may be obtained in large quantity from the lead salt. From each kilogram of the salt there were obtained about 80 grams of the new body. It is a light, limpid, very mobile oil, with a slight odor suggesting that of benzene. It does not solidify in a mixture of ice and salt. It dissolves in concentrated sulphuric acid, the solution being of a deep brown color. When the oil is treated with bromine it yields a product of the formula $C_4H_2Br_2S$, which in odor and other general properties closely resembles bibrombenzene. The monobrom derivative, the sulphonic acid, the sulphochloride, sulphamide and the carbonic acid of the new body also resemble the corresponding derivatives of benzene. Thus apparently an extensive new field is opened, the cultivation of which will yield a large number of interesting bodies, the properties of which will be similar to those of the corresponding derivatives of benzene. Their constitution will also be similar, only instead of from benzene they will be derived from a mother substance containing sulphur. For the latter the author proposes the name *thiophene*. In addition to the properties above stated, the following may be mentioned: It is stable towards alkalis and even the alkali metals. It remains unchanged when boiled for hours over sodium. Nitric acid oxidises it with violent action.

All commercial benzene contains thiophene. An estimation of sulphur in a specimen of the purest coal tar benzene indicated the presence of about 0.5 per cent.

It would be premature to attempt to determine the constitution of the new body at present. The analogy between the formulas of thiophene, C_4H_4S , and furfuran, C_4H_4O , is suggestive, and, further, the striking similarity between the derivatives of thiophene and benzene. The author suggests that thiophene may be benzene

in which two CH groups are replaced by an atom of sulphur.—
(*Berichte der deutschen chemischen Gesellschaft*, 16, 1465.)

The Preparation of Aluminium.

According to a statement in the *Bulletin de la Société de l'industrie minérale*, 2, 451, Salindres is at present the only factory in which aluminium is manufactured. The quantity manufactured is about 2400 kilograms annually. The sodium is prepared by igniting sodium carbonate with charcoal and a little lime to facilitate the distillation, the requisite chlorides of aluminium and sodium by distilling a mixture of alumina, charcoal and sodium chloride in a current of chlorine. The distilled double salt is then melted together with sodium and some cryolite to serve as a flux.

Recently the statement has been current in a number of journals that material improvements have been made in the manufacture of aluminium at the *Aluminium Crown Metal Works*, in Hollywood, which are under the direction of J. Webster. It is said that a ton of the metal costs now only 2000 marks (\$500), while it formerly cost 20,000 marks (\$5000). According to the latest statement on the subject, the new method consists in igniting bauxite with sodium carbonate, decomposing the sodium aluminate with carbon dioxide, heating the separated alumina with charcoal in a current of chlorine, and melting with sodium and cryolite the double chloride of sodium and aluminium thus obtained.

It does not appear probable that by this method, which is essentially an old one, a kilogram of aluminium can be made for two marks, or indeed even for 20 marks.

J. Webster, in Solihul (Austrian Patent, Sept. 28th, 1882), describes the following *method for the preparation of alumina for the purpose of manufacturing aluminium*. 3 parts of alum are mixed with 1 part of coal pitch, and the mixture heated to 200 to 260°. In about three hours the pasty mass is spread upon a stone floor, and, after it has become cool, it is broken in pieces. Hydrochloric acid of 20 to 25 per cent. is poured upon these pieces placed in piles, which are from time to time turned over. When the evolution of sulphuretted hydrogen has stopped, charcoal powder or lamp black to the extent of about 5 per cent. and enough of water to make a thick mass are added. The mass is thoroughly broken up and mixed in a mill, and then worked into balls of about 0.5 kilogram each. These are bored through to facilitate drying, and heated in a drying chamber at first to 40°, then in a furnace at 95 to 150°. The balls are now kept for three hours at a low red heat in retorts, while a mixture of two parts water vapor and one part air is passed through, so that sulphur and charcoal are converted into sulphur dioxide and carbon dioxide and thus escape. The current of gases carries over some potassium sulphate, ferric

sulphate and alumina, and is hence brought into clay condensers. After the substances mentioned have been driven off, the dry residue is removed from the retort and cooled, again placed in the mill and ground to a fine powder, which consists of aluminium oxide and potassium sulphate. This powder is treated with about seven times its weight of water, then boiled in a pan or boiler by means of steam for about an hour, and allowed to stand until cool. The solution containing potassium sulphate is run off, and evaporated to dryness; the alumina is washed out and dried.

J. Morris, of Uddington, near Glasgow (German Patent, No. 22150, August 30, 1882), claims to obtain *aluminium by treating an intimate mixture of alumina and charcoal with carbon dioxide*. For this purpose a solution of aluminium chloride is mixed with powdered wood, charcoal and lamp black, then evaporated, until it forms a viscous mass, which is shaped into balls. During the evaporation hydrochloric acid is given off. The residue consists of alumina intimately mixed with charcoal. The balls are dried, then treated with steam in appropriate vessels for the purpose of driving off all the chlorine, care being taken to keep the temperature so high that the steam is not condensed. Now the temperature is raised, so that in the dark the tubes are seen to be at low red, and dry carbon dioxide then passed through. This is said to be reduced by the charcoal to carbon monoxide, which now, as affirmed by Morris, reduces the alumina to aluminium.

Although the quantity of the escaping carbon monoxide is in general a good indication of the progress of the reduction, it is nevertheless advisable not to continue the heating of the tubes or vessels until the evolution of this gas has ceased or even nearly ceased, as, in consequence of slight differences in the consistence of the balls, some of them give up all their carbon sooner than the others. The treatment of the balls with carbon dioxide for the purpose of the reduction lasts about 30 hours, when the substances are mixed in the proportions of 5 parts carbon to 4 parts alumina.

As Morris states, further, the metal appears as a porous, spongy mass. It is freed from the residual alumina and particles of charcoal by fusion and mechanical treatment and then poured into molds.—(*Dingler's Polytechnisches Journal*, 249, 86.)

RECENT PUBLICATIONS RELATING TO CHEMISTRY.

I.—AMERICAN.

- BLOXAM, C. L. Chemistry, inorganic and organic, with experiments. 5th Ed. Philadelphia: Blakiston.
- BROWN, W. L. Manual of assaying gold, silver, copper, and lead ores. Chicago: Jansen, McClurg & Co.
- GRIFFIN, LA ROY F. Lecture notes in chemistry: a syllabus compiled principally from the manuals of Miller and of Roscoe and Schorlemmer. Philadelphia: Sower, Potts & Co.
- HOFFMANN, F., and POWER, F. B. A manual of chemical analysis as applied to the examination of medicinal chemicals and their preparations. 3d Ed., entirely rewritten and enlarged. Phila.: H. C. Lea's Sons & Co.
- MITCHELL, C. Practitioner's guide to urinalysis. Chicago: Gross & Delbridge.
- PINNER, A. Introduction to organic chemistry. Translated and revised by P. T. Austen. N. Y.: Wiley.
- SHERRERD, J. M. Iron analysis record. Troy: Young.
- SOUTHWICK, A. P. Question book of chemistry. Syracuse: Bardeen.
- STODDARD, J. T. An outline of qualitative analysis for beginners. Northampton: Gazette Printing Office.

II.—ENGLISH.

- FENTON, H. J. H. Notes on qualitative analysis, concise and explanatory. London: Cambridge Warehouse.
- FRANKLAND, P. F. Agricultural chemical analysis. London: Macmillan.
- MORGAN, C. L. Water: its teachings in chemistry, physics, and physiology. London: Stamford.
- RIDSDALE, C. H. Chemical percentage tables and laboratory calculations. London: Crosby & Lockwood.

III.—FRENCH.

- BOUANT, E. Cours de physique et de chimie, rédigé conformément au programme des écoles normales primaires d'instituteurs. Paris: Delalain.
- CLAPARÉDE, A. Quelques nouvelles kétones aromatiques obtenue par condensation moléculaire. Genève.
- DELAURIER, E. Essai d'une théorie générale supérieure de philosophie naturelle et de thermochimie, avec une nouvelle nomenclature binaire notative pour la chimie minérale et organique. Fasc. I. Paris: imp. Lahure.
- DOCUMENTS sur les falsifications des matières alimentaires et sur les travaux du laboratoire municipal. Paris: Masson.
- FABRE, E. Étude sur les eaux minérales de Caprem. Paris: Davy.
- GIRARDIN, J. Leçons de chimie élémentaire appliquée aux arts industriels. Tom. III. Chimie organique. Paris: Masson.
- KLEIN, D. Sur les acides borotungstiques. Paris: Gauthier-Villars.

- LEPLAY, H. Chimie théorique et pratique des industries du sucre. T. I. Paris: Baudoin.
- MORELLE, E. Recherches chimiques sur la bergénite. Lille: Danel.
- PELIGOT, E. Traité de chimie analytique appliquée à l'agriculture. Paris: Masson.
- PELLET, H., et SEUGIER, G. La fabrication du sucre. Tom. I. Paris: Pellet.
- PISANI, F., et DERVELL, P. La chimie du laboratoire. Paris: Baillière.
- POIRÉ, P. Leçons de chimie. Paris: Delagrave.
- SCHUTZENBERGER, P. Traité de chimie générale, comprenant les principales applications aux sciences biologiques et aux arts industriels. Tome III. Paris: Hachette.
- THOMAS, A. Manuel de l'alcoômetrie. Lille: Michelet.

IV.—ITALIAN.

- SBRIZIOLO, M. Trattato di chimica analitica qualitativa ed quantitativa. Napoli: Eschera.
- SBRIZIOLO, M. Trattato di chimica generale inorganica ed organica. Napoli.

V.—SCANDINAVIAN.

- SCHMELCK, L. Chemistry of the Norwegian North-Atlantic Expedition. 1. On the solid matter in sea water. 2. On oceanic deposits. Christiania.

VI.—GERMAN.

- BEILSTEIN, F. Handbuch der organischen Chemie. Leipzig: Voss.
- BERGHAUS, A. Das Glycerin, seine Gewinnung und Verwendung in der Industrie. Berlin: Pohl.
- ELSNER, F. Recepte für Pharmacie und chemische Grossindustrie. Halle: Knapp.
- FLÜCKIGER, F. A. Die Chinarinden. In pharmakognostischer Hinsicht dargestellt. Berlin.
- GROSHANS, J. A. Ein neues Gesetz analog zu dem Gesetz von Avogadro. Deutsch von F. Roth. Leipzig: Barth.
- HOFMANN, A. W. Chemische Erinnerungen aus der Berliner Vergangenheit. Zwei akademische Vorträge. Berlin.
- HAUSSKNECHT, O. Lehrbuch der Chemie und chemischen Technologie. Hamburg.
- KAYSER, H. Lehrbuch der Spectralanalyse. Berlin: Springer.
- KOLBE, H. Lehrbuch der organischen Chemie. Braunschweig.
- KÜNSTLE, G. Kohlenstoff-Skizzen. Ein organisch-chemisches Hohes Lied. München.
- LEDEBUR, A. Die Metallverarbeitung auf chemisch-physikalischem Wege. Braunschweig: Vieweg.
- LIPPMANN, E. O. v. Die Zuckerarten und ihre Derivate. Vom Vereine für die Rübenzucker-Industrie des Deutschen Reiches mit dem ersten Preise gekrönte Monographie. Braunschweig.
- LOEW, O., und BOKORNY, T. Die chemische Kraftquelle im lebenden Protoplasma. Muenchen.

- MEDICUS, L. Kurze Anleitung zur Massanalyse. Im Anschlusse an die "Kurze Anleitung zur qualitativen Analyse." Mit specieller Berücksichtigung der Vorschriften der Pharmakopöe bearbeitet. Tübingen.
- MEYER, L., und SEUBERT, K. Atomgewichte der Elemente aus den Originalzahlen neu berechnet. Leipzig: Breitkopf und Härtel.
- PALM, R. Grundriss der qualitativen und quantitativen chemischen Analyse, nebst einer General-Tabelle der wichtigsten Pflanzen-Alkaloide und einer Spectral-Tafel. Leipzig.
- RASPE, FR. Heilquellen-Analysen für normale Verhältnisse und zur Mineralwasserfabrikation, berechnet auf zehntausend Theile. 1 Lieferg. Dresden.
- RIETH. Volumetrische Analyse. Hamburg.
- SCHAEGLER, C. Die Technologie der Fette und Oele des Thier- und Pflanzenreichs. Berlin.
- SCHMID, A. E. v. Leitfaden für den Unterricht in ausgewählten Kapiteln der chemischen Technologie. Graz.
- SCHULTZ, G. Die Chemie des Steinkohlentheers mit besonderer Berücksichtigung der künstlichen organischen Farbstoffe. Braunschweig.
- SCHWANERT, H. Lehrbuch der pharmaceutischen Chemie. In 3 Bdn. Braunschweig: Schwetschke und Sohn.
- SCHWACKHÖFER, F. Lehrbuch der landwirthschaftlich-chemischen Technologie mit besonderer Berücksichtigung der österreichischen Verhältnisse. Zum Gebrauche an landwirthschaftlichen u. technischen Lehranstalten, sowie für Landwirthe, Industrielle, Steuerbeamte, etc.
- WINKLER, CL. Die Maassanalyse nach neuem titrimetrischem System. Kurzgefasste Anleitung zur Erlernung der Titrimethode. Der chemischen Anschauung der Neuzeit gemäss bearbeitet. Freiberg.
- ZAENGERLE, M. Grundriss der Chemie und Mineralogie. Nach den neuesten Ansichten der Wissenschaft für den Unterricht an Mittelschulen, besonders Gewerbe-, Handels- und Realschulen bearbeitet. I Theil. Anorganische Chemie und Mineralogie. Braunschweig.

*UNIVERSITY PUBLICATIONS.**JENA.*

- JAMES, W. Ueber die Derivate des Aethylen chlorobromids; insbesondere über das Aethylen chloresulfocyanat und seine Reactionen.
- KNORRE, G. v. Beiträge zur Kenntniss der Wolframverbindungen.
- SCHEID, B. Beiträge zur Kenntniss des Benzo-chinons.

F. W. C.